

The Crystal Structure of Quartz-like GeO₂

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The atomic parameters of the quartz form of germanium dioxide have been determined at room temperature from diffractometrically measured intensities with Mo $K\alpha$ radiation. Initial values of the parameters were obtained by Fourier techniques, and the anisotropic refinement was carried out by least-squares analysis to the unusually low R value of 1.9%. The two independent Ge–O bond lengths are 1.737 ± 0.003 and 1.741 ± 0.002 Å; the independent O–Ge–O bond angles are 106.3 ± 0.1 ; 107.7 ± 0.2 , 110.4 ± 0.1 and $113.1 \pm 0.1^\circ$. The irregularity in the GeO₄ tetrahedron is thus clearly attributable to distortions in the bond angles. The Ge–O–Ge bond angle of $130.1 \pm 0.1^\circ$ is significantly smaller than the corresponding angle in SiO₂. Analysis of the thermal ellipsoid data indicates that the vibration of germanium is very nearly isotropic; that of oxygen definitely anisotropic. The maximum r.m.s. displacement of oxygen is, as in SiO₂, perpendicular to the plane defined by the given oxygen and the two germanium atoms which it links.

Introduction

Germanium dioxide exhibits an interesting and comparatively rare type of polymorphism in having two room-temperature-persistent forms of differing anion coordination about the central cation. One modification is of the α -quartz type (Zachariasen, 1928) and thus has 4:2 coordination; the other form, of the rutile type (Laubengayer & Morton, 1932), accordingly has 6:3 coordination. These latter investigators have shown quartz-like GeO₂ to be actually the stable high-temperature phase. However, the transformation in the absence of hydrothermal conditions is quite sluggish. In contrast with the relative ease of preparation of these forms of GeO₂, the rutile modification of silicon dioxide, stishovite, is formed under conditions of extremely high pressure (Stishov & Popova, 1961). It should be pointed out, however, that the cation/anion radius ratio for GeO₂ is exceedingly close (Pauling, 1960) to the limiting value of 0.414 for the transition from tetrahedral to octahedral coordination, but this is not the case for SiO₂.

A previous analysis (Smith, 1963) of AX₂ quartz-like compounds set forth the conditions imposed on the unit-cell dimensions if the AX₄ tetrahedra be strictly regular. One of the results was that the axial ratio is then required to be less than 1.0981 ($=\frac{3}{2}(\sqrt{3}-1)$) in the α phase and equal to 1.0981 in the β phase, the latter value thus being a fixed number, independent of temperature. Published values of the lattice constants indicated that at room temperature the GeO₄ tetrahedra are considerably more irregular than the SiO₄ tetrahedra. However, the analysis does not of itself distinguish between an irregularity caused by unequal bond distances, unequal X–A–X bond angles or a combination of both. Accordingly this

point is now settled by the structure determination herewith reported.

Experimental

Our sample of (synthetic) germania quartz, kindly supplied by Drs F. Dachille and R. Roy of Pennsylvania State University, consisted of mostly small (≤ 0.10 mm), irregularly shaped crystals, otherwise colorless and free of adhering material. Single-crystal oscillation and Weissenberg photographs confirmed the trigonal symmetry and led to lattice constants in excellent agreement with the powder-diagram values, $a=4.987$ and $c=5.652$ Å, reported by Swanson & Tatge (1953). These latter values were in fact used in the succeeding computations.

The intensity measurements were carried out at room temperature on a G.E. XRD5 spectrometer equipped with a goniostat, scintillation counter and pulse-height discrimination circuitry; the radiation employed was niobium-filtered Mo $K\alpha$. Several crystals were tested on this arrangement before one (an irregularly shaped chip $\sim 0.11 \times 0.09 \times 0.08$ mm) was found which yielded an altogether satisfactory agreement among the intensities of equivalent reflections. In fact, with this crystal 9 of 10 pairs of equivalent reflections of the type $hk0$ and $kh0$ gave $|F_o|$'s which on the average deviate from the pair-average by 0.6%; only the rather weak reflections 340 and 430 gave an exceptional deviation (2.7%) from their mean.

The only other thing of an unusual nature in measuring the intensities was that the I_i/I_p curve (Alexander & Smith, 1962) was found to have a χ dependence throughout the 2θ range of interest. An examination of the instantaneous diffraction images by means of the combination photographic and counter technique of Alexander, Smith & Brown

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(1963) revealed that the crystal was split into two components, each of which was nearly perfect ('mosaic spread' $\leq 0.05^\circ$, the precision of the method) and one misoriented with respect to the other by $\sim 0.07^\circ$ in ω . The intensities were therefore measured almost exclusively by the 2θ -scan method, the exceptions being a few of the very faint reflections which were measured as net peak heights and then converted to integrated intensities by means of an experimental I_i/I_p curve appropriate to the particular χ and 2θ . A total of 194 reflections, of which 193 were distinctly above background, were recorded up to a 2θ cutoff of $\sim 68^\circ$. These were converted to a set of relative $|F_o|$'s by the application of Lorentz and polarization factors. Probable errors in the $|F_o|$'s were estimated directly from the recorded counts in a manner previously described (Smith & Alexander, 1963). At a later stage the absorption corrections (*International Tables for X-ray Crystallography*, 1962) appropriate for a spherical crystal of $\mu R = 1.1$ were applied.

Determination of the structure

Of the two enantiomorphous space groups compatible with the diffraction effects we have chosen to describe the structure in terms of $P3_221$ (instead of $P3_121$), and in order to facilitate a ready comparison with the results for α quartz, we employ the convention of Wyckoff (1948) that a crystallographic twofold axis coincides with the a axis of the trigonal unit cell. The one independent oxygen is in a general position and the independent germanium atom thus occupies the special position, $x, 0, 0$. Including a scale factor and anisotropic temperature factors, a total of 15 parameters are to be determined from the 194 measured reflections.

Preliminary values for all four positional coordinates were obtained from Patterson and electron-density projections onto a plane perpendicular to the twofold axis. This projection shows the structure with good resolution and is centrosymmetric, although the structure as a whole is not. Several cycles of difference syntheses provided improved values for the coordinates as well as isotropic temperature factors for each atom.

Final refinement was carried out on our entire data using the least-squares program of Busing & Levy

(1959) and employing a weighting scheme based on the aforementioned probable errors in the observed structure factors. The scattering factors were those given in *International Tables for X-ray Crystallography* (1962) for the neutral atoms. Three cycles of least squares on data uncorrected for absorption produced convergence and reduced the overall R value based on $|F|$ from 6.9% to 2.0%. Inasmuch as the absorption correction factors for a spherical crystal cause a maximum variation of about 7% (in $|F|$) for the range of 2θ encountered, it was decided to apply these corrections and to then repeat the refinement, lest a systematic trend be introduced into our results. Two further cycles on the corrected data produced negligible changes in the positional coordinates and lowered the R value only to 1.9%. The standard deviations, however, were nearly uniformly 11% lower than their values for the uncorrected data; furthermore, the 'error of fit' figure decreased from 1.71 to 1.47, a reduction of 16%. It is clear then that the absorption corrections allow a substantially better 'fit' between observed and calculated $|F|$'s, although for some reflections these corrective factors may still not be entirely satisfactory for the actual crystal. The parameters from the last cycle on the absorption-corrected data were therefore accepted as final and are listed in Table 1.

The overall excellent agreement between the observed and calculated structure factors in Table 2 precludes a substantial amount of either primary extinction or Dauphiné twinning, which on the basis of behavior of both synthetic and natural quartz crystals might also have been expected in the GeO_2 crystal used here. [For further details concerning the frequent effects of marked primary extinction in quartz, the reader is referred to Brill, Hermann & Peters (1949, 1942) and to Young & Post (1962) (hereafter designated YP); for Dauphiné twinning, Smith & Alexander (1963) (hereafter designated SA).] To be sure, the presence of some amount of extinction is indicated in three of the most intense reflections, 011, 003 and 102, but short of reducing the R value to 1.6% no significant changes in the structural parameters are to be expected on this account. On the other hand, the 1.6% value is perhaps a truer measure of the excellence of our intensity measurements.

Table 1. *Final values of the parameters from least-squares refinement on absorption-corrected intensity data.*

Estimated standard deviations in parentheses									
	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O	0.3969 (0.0005)	0.3021 (0.0005)	0.0909 (0.0004)	0.0192 (0.0011)	0.0142 (0.0010)	0.0083 (0.0005)	0.0118 (0.0010)	-0.0037 (0.0007)	-0.0034 (0.0006)
Ge	0.4513 (0.0001)	0 —	0 —	0.0076 (0.0002)	0.0067 (0.0002)	0.0042 (0.0001)	$=\beta_{22}/2$ —	-0.0001 ₁ (0.0000 ₅)	$=2\beta_{13}$ —

Table 2. Observed and calculated structure factors.

Calculated values, based on $F_{000}=288$, are scaled to the observed values by the factor $K=1.594 \pm 0.006$

h k l	10 F _o	10 F _c	h k l	10 F _o	10 F _c	h k l	10 F _o	10 F _c	h k l	10 F _o	10 F _c	h k l	10 F _o	10 F _c	h k l	10 F _o	10 F _c
0 0 3	1867	2025	0 5 3	320	314	1 3 2	946	949	2 2 0	1015	995	3 1 4	559	555	4 2 0	504	500
0 0 6	959	970	0 5 4	796	802	1 3 3	1075	1083	2 2 1	892	916	3 1 5	374	361	4 2 1	885	907
0 0 9	745	756	0 5 5	96	77	1 3 4	387	381	2 2 2	671	674	3 1 6	674	677	4 2 2	351	362
0 1 1	2504	2478	0 6 1	43	34	1 3 5	710	702	2 2 3	949	944	3 2 0	513	505	4 2 3	311	306
0 1 2	195	220	0 6 2	881	892	1 3 6	656	653	2 2 4	781	755	3 2 1	444	440	4 2 4	655	666
0 1 3	857	840	1 0 0	971	953	1 4 0	693	686	2 2 5	641	621	3 2 2	989	992	4 3 0	216	196
0 1 4	1451	1436	1 0 1	1284	1309	1 4 1	587	561	2 2 6	673	671	3 2 3	171	167	4 3 1	489	492
0 1 5	787	795	1 0 2	1770	1890	1 4 2	637	685	2 3 0	509	505	3 2 4	455	448	4 3 2	656	646
0 1 6	323	318	1 0 3	466	397	1 4 3	737	733	2 3 1	1232	1217	3 2 5	833	848	4 3 3	271	266
0 1 7	775	784	1 0 4	1304	1324	1 4 4	466	477	2 3 2	361	350	3 2 6	155	153	4 4 0	298	276
0 1 8	558	555	1 0 5	1108	1119	1 4 5	606	601	2 3 3	451	451	3 3 0	1198	1186	5 0 0	242	243
0 2 1	615	604	1 0 6	377	369	1 5 0	841	852	2 3 4	1056	1053	3 3 1	136	125	5 0 1	409	410
0 2 2	1031	1011	1 0 7	411	412	1 5 1	355	355	2 3 5	347	356	3 3 2	67	42	5 0 2	1056	1079
0 2 3	1377	1382	1 0 8	698	709	1 5 2	377	384	2 3 6	130	120	3 3 3	935	932	5 0 3	357	334
0 2 4	159	129	1 1 0	1312	1255	1 5 3	789	802	2 4 0	511	500	3 3 4	226	218	5 0 4	270	268
0 2 5	729	716	1 1 1	1125	1112	1 6 0	328	347	2 4 1	519	508	3 4 0	205	196	5 0 5	799	818
0 2 6	1044	1051	1 1 2	1319	1307	1 6 1	604	625	2 4 2	840	824	3 4 1	631	620	5 1 0	831	852
0 2 7	289	291	1 1 3	1049	1058	2 0 0	1928	1948	2 4 3	334	327	3 4 2	367	378	5 1 1	425	414
0 3 1	2139	2202	1 1 4	1028	1022	2 0 1	348	370	2 4 4	480	472	3 4 3	279	279	5 1 2	434	426
0 3 2	256	258	1 1 5	944	945	2 0 2	1029	1034	2 5 0	388	409	3 5 0	586	582	5 1 3	702	697
0 3 3	71	67	1 1 6	707	716	2 0 3	1798	1871	2 5 1	545	551	4 0 0	654	656	5 2 0	394	409
0 3 4	1194	1193	1 1 7	653	656	2 0 4	569	560	3 0 0	0	62	4 0 1	1132	1213	5 2 1	369	377
0 3 5	197	194	1 1 8	454	453	2 0 5	239	237	3 0 1	121	115	4 0 2	345	350	5 2 2	578	582
0 3 6	150	149	1 2 0	678	665	2 0 6	964	970	3 0 2	1804	1852	4 0 3	935	947	6 0 0	62	62
0 3 7	703	718	1 2 1	936	918	2 0 7	491	495	3 0 3	194	194	4 0 4	832	829	6 0 1	862	874
0 4 1	341	346	1 2 2	1686	1731	2 1 0	679	665	3 0 4	98	92	4 0 5	398	405	6 0 2	56	68
0 4 2	1059	1040	1 2 3	454	451	2 1 1	1622	1627	3 0 5	943	958	4 0 6	527	530	6 1 0	340	347
0 4 3	503	500	1 2 4	441	441	2 1 2	509	494	3 0 6	135	130	4 1 0	651	686	6 1 1	278	286
0 4 4	462	465	1 2 5	1065	1051	2 1 3	1019	1015	3 0 7	164	160	4 1 1	814	830	7 0 0	479	478
0 4 5	689	693	1 2 6	565	561	2 1 4	1150	1133	3 1 0	1400	1410	4 1 2	613	603			
0 4 6	593	593	1 2 7	189	180	2 1 5	235	237	3 1 1	505	503	4 1 3	569	563			
0 5 1	884	902	1 3 0	1406	1410	2 1 6	500	491	3 1 2	523	532	4 1 4	713	724			
0 5 2	122	125	1 3 1	505	507	2 1 7	763	769	3 1 3	1085	1065	4 1 5	447	464			

Discussion

The general character of the atomic arrangement in quartz-like GeO₂ is most easily visualized by reference to Fig. 1. Every Ge atom lies on a crystallographic twofold axis and is surrounded by four O in tetrahedral coordination; each O thereof is shared between two

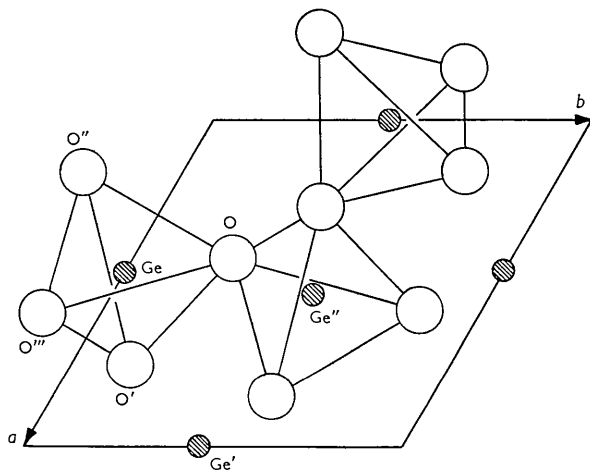


Fig. 1. Atomic arrangement in quartz-like GeO₂ viewed along the *c* axis. The oxygen tetrahedra are outlined with solid lines.

germanium atoms, a three-dimensional framework thus being formed. In addition to the two Ge atoms, each O is contact with six oxygen atoms of the linked-tetrahedra system.

Table 3 summarizes the bond data. It is seen that the values for the two independent Ge-O bond lengths, 1.737 ± 0.003 and 1.741 ± 0.002 Å, are in excellent agreement with one another. As explained earlier, the observed value of the axial ratio indicates that

Table 3. Interatomic distances and bond angles in germania quartz

Standard deviations in parentheses

	Length	Angle
Ge-O	1.737 Å (0.003)	O-Ge-O''' 106.3° (0.1)
Ge-O'	1.741 (0.002)	O-Ge-O'' 107.7 (0.2)
O-O'''	2.783 (0.002)	O'-Ge-O''' 110.4 (0.1)
O-O''	2.805 (0.004)	O-Ge-O' 113.1 (0.1)
O'-O'''	2.860 (0.004)	
O-O'	2.902 (0.003)	Ge-O-Ge'' 130.1 (0.1)
Ge-Ge''	3.1534 (0.0001)	

the GeO₄ tetrahedra in germania quartz are necessarily irregular; it now follows that the source of the irregularity is almost entirely confined to the O-Ge-O bond angles, which Table 3 shows range from 106.3° to 113.1°. This behavior contrasts with that in SiO₂ quartz, where the room temperature bond data* led to the suggestion (Smith, 1963) that some of the irregularity within the tetrahedra is due to (slightly) dissimilar Si-O bond distances.

It is of interest to contrast further the bond data of these two quartz structures. While the GeO₄ tetrahedra are more irregular with respect to bond angles, the longer Ge-O bond lengths actually result in a much more satisfactory set of O...O contacts within a given tetrahedron. From Table 3 we see that these distances are mostly in excess of 2.80 Å (*i.e.* twice the packing radius for O); in contrast, the corresponding distances in SiO₂ quartz average to 2.624 Å. The bond angle at the O atoms moreover is decidedly different in the two compounds, 130.1° for Ge-O-Ge *versus* 144.0° for Si-O-Si. In terms of

* The bond data of interest are: Si-O, 1.597 ± 0.003 , 1.617 ± 0.003 Å; O-Si-O, 110.3, 109.5, 109.2, 108.8° (all $\pm 0.2^\circ$) from natural quartz (SA, 1963); Si-O, 1.603 ± 0.003 , 1.611 ± 0.003 Å; O-Si-O, 110.1, 110.0, 109.2, 108.7° (all $\pm 0.2^\circ$) from synthetic quartz (YP, 1962).

Table 4. Atomic thermal ellipsoids for germania quartz.

Notation as in Smith & Alexander (1963)

Germanium						
	u_1 or φ_1	σ	u_2 or φ_2	σ	u_3 or φ_3	σ
u	0.0785 Å	0.0013 Å	0.0831 Å	0.0012 Å	0.0866 Å	0.0012 Å
u_x	0	0	0	0	0.0866	0.0012
u_y'	-0.071	0.005	-0.035	0.012	0	0
u_z	-0.033	0.011	0.075	0.006	0	0
φ_x	90.0°	0.0°	90.0°	0.0°	0.0°	0.0°
φ_y'	155.1	9.1	114.9	9.1	90.0	0.0
φ_z	114.9	9.1	24.9	9.1	90.0	0.0
Oxygen						
	u_1 or φ_1	σ	u_2 or φ_2	σ	u_3 or φ_3	σ
u	0.090 Å	0.004 Å	0.104 Å	0.005 Å	0.147 Å	0.004 Å
u_p	-0.032	0.020	0.097	0.010	0.009	0.009
u_q	0.002	0.005	-0.006	0.007	0.147	0.004
u_r	0.084	0.009	0.037	0.023	-0.001	0.008
φ_p	110.7°	13.8°	21.0°	13.6°	86.6°	3.7°
φ_q	88.6	3.2	93.1	3.7	3.4	3.6
φ_r	20.7	13.8	69.3	13.8	90.2	3.3

expansion of the framework structure, increase in the bond lengths and closure of the oxygen bond angles are, of course, offsetting factors. Comparing GeO_2 with SiO_2 , we thus find that the percentage increase in the unit-cell dimensions of GeO_2 corresponds to an average linear expansion of only about 2.5%, despite a percentage increase in the Ge-O bond length of about 8.2% (0.13 Å).

Very few experimental bond data are available for comparison with the present results. Nowotny & Szekely (1952) report tetrahedral Ge-O bond distances in SrH_2GeO_4 (isotypic with KH_2PO_4) of 1.73 Å. In contrast, Ginetti (1954) finds Ge-O distances of 1.84-1.85 Å in Na_2GeO_3 (isotypic with Na_2SiO_3). In neither study, however, are the limits of errors given. It is especially interesting to note that the Ge-O-Ge angle along the chain in $\text{Na}_2\text{GeO}_3^*$ is considerably smaller (110°) than the corresponding angle (137°) in Na_2SiO_3 (Grund & Pizy, 1952). While this difference of 27° in the bond angles may be subject to considerable uncertainty due to the limited accuracy of these older studies, the results, taken with our present findings, suggest that the germanates, as compared with the corresponding silicates, will be generally characterized by smaller bond angles at oxygen.

The dimensions and orientations of the thermal vibration ellipsoids of the germanium and oxygen atoms are presented in Table 4 and in Figs. 2 and 3. Reference axes are the same as those employed by SA and YP for SiO_2 . Thus, the axes X, Y', Z in Fig. 2 form an orthogonal set, of which X and Z coincide respectively with a and c , while Y' is normal to both X and Z . Since a is an axis of twofold sym-

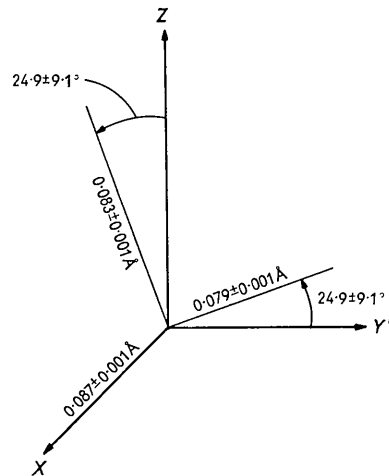


Fig. 2. Principal axes of the thermal vibration ellipsoid of germanium. Distances in Å are the r.m.s. displacements.

metry, one of the principal axes of the germanium ellipsoid is obliged to lie along X . Orientation of the thermal ellipsoid for O is referred to the orthogonal axes, p, q, r , which are determined by the three atoms Ge, O, Ge'' as indicated in Fig. 4. Table 5 compares the magnitudes of the principal axes with those in SiO_2 .

The outstanding feature of these results for the germanium atom is the close approach to isotropy of thermal vibration. This near isotropy renders the apparent tilt of the ellipsoid away from the Y', Z axes of doubtful significance, although the angle of departure is in fact nearly 2.7σ . By way of comparison, the silicon atom in α quartz undergoes a considerably more anisotropic motion, the largest r.m.s. displacement of which is along Z , whereas the major axis in GeO_2 marginally is along X . Surprisingly enough,

* The account in *Structure Reports*, 18, 447 (1954) concerning this compound contains a typographical error. The c axis repeat distance should read 4.92 Å, not 9.92 Å.

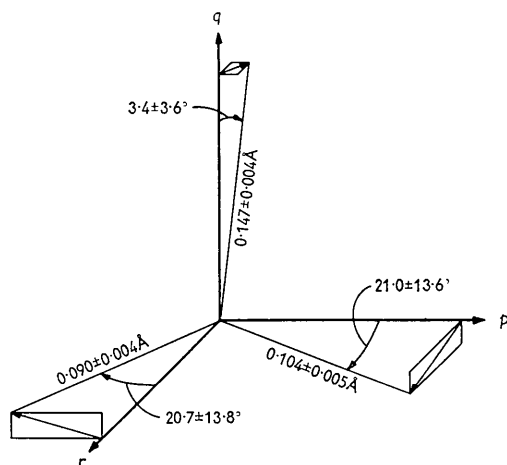


Fig. 3. Principal axes of the thermal vibration ellipsoid of oxygen. Distances in Å are the r.m.s. displacements. See Fig. 4 for orientation of reference axes p, q, r .

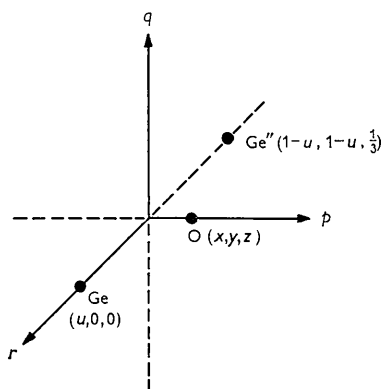


Fig. 4. Orientation of the reference axes pqr . See Fig. 3.

Table 5. Comparison of thermal ellipsoids for germania quartz with those in α quartz

	Ge	Si	
		SA	YP
u_1	0.079 ± 0.001 Å	0.051 ± 0.007 Å	0.049 ± 0.005 Å
u_2	0.087 ± 0.001	0.074 ± 0.005	0.072 ± 0.004
u_3	0.083 ± 0.001	0.080 ± 0.004	0.086 ± 0.003
	O		
u_1	0.090 ± 0.004 Å	0.084 ± 0.008 Å	0.052 ± 0.008 Å
u_2	0.104 ± 0.005	0.102 ± 0.007	0.099 ± 0.005
u_3	0.147 ± 0.004	0.132 ± 0.006	0.134 ± 0.004

(SA=Smith & Alexander, 1963; YP=Young & Post, 1962).

the r.m.s. displacements are somewhat larger for germanium than for silicon, despite the larger mass of germanium. It would therefore seem to follow

that the larger sized GeO₄ tetrahedra allow a thermal motion for the central atom which is less restrictive as to amplitude and particularly less restrictive with regard to direction.

A comparison of the oxygen ellipsoid data between the two structures is more difficult because, among other things, the results of YP and SA are not in total agreement (note in Table 5 the discrepancy between the u_1 values for O; see also SA for details concerning the differences in orientation). Furthermore the two compounds differ appreciably with regard to the bonding system about the oxygen atom. Nonetheless, the integrated picture is one of more similarities than differences. Thus, the oxygen thermal ellipsoid, as in SiO₂, appears to coincide with the molecular axes, p, q, r , due consideration being given to the standard deviations (Fig. 3). The relative ease of vibration, as judged by the magnitudes of the principal axes, is likewise in the same order with respect to p, q, r . Perhaps the only change associated with the differing bond configuration is a closer approach to isotropy in the p, r plane (the expected result of a smaller bond angle) and a greater amplitude in the q direction.

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