atoms at 100 K also show that motion in the *ab* plane is of larger amplitude than motion along *c*. At 205 K, the deuterium thermal ellipsoid in ND_4ReO_4 becomes very elongated along *a*, suggesting high-amplitude librational motion about *c*. Preferred reorientation of the NH_4^+ ions about *c* at 4·2 K was demonstrated by Lalowicz, McDowell, Raghunathan & Srinivasan (1978) by proton magnetic resonance. The presence of large-amplitude *c*-axis librations of the ammonium ion at 205 K is also consistent with the broadening and disappearance of the ammonium ion lattice modes in the Raman spectra in the vicinity of 200 K (Korppi-Tommola, Devarajan, Brown & Shurvell, 1978), and suggests that higher librational-rotational energy levels become significantly populated at about this temperature. Petch, Reynhardt & Watton (1978) proposed a similar model in which general reorientation of the ammonium ion takes place at temperatures above 100 K. The present results indicate that ammonium ion rotational motion remains restricted until temperatures above 200 K are reached.

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Straight Si—O—Si Bridging Bonds Do Exist in Silicates and Silicon Dioxide Polymorphs

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Abstract

In 109 precisely determined crystal structures 247 different SiO_4 tetrahedra have been found which have a total of 293 unique O atoms involved in bridging Si—O—Si bonds. Eight of the O atoms are located on symmetry elements and have straight bridging angles of 180°. In four more cases of essentially straight Si—O—Si angles (177·7 to 179·9°) the O atoms are located in less symmetrical positions. The number of straight angles is surprisingly large if one considers the frequency of their occurrence per unit solid angle. The frequency distribution corrected per unit solid angle of the bridging angle in silicates has peaks at 139, 157 and 180° (with a mean of 154°), while the silica polymorphs have peaks at 147, 157 and 180° (with a mean of 162°). The latter distribution is different from the distribution found experimentally for vitreous silica.

Introduction

About twenty years ago Liebau (1961) studied the question as to whether or not the angle Si—O—Si in silicates can assume a value of 180°. The answer given then was that normally the average value of the

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bridging angle Si—O—Si is 140°. In cases where angles of 180° were reported they seemed to be apparent, that is, caused by a pseudosymmetry in the crystal structure. The actual space-group symmetry of the structures in question was believed to be lower, thus allowing bridging angles of less than 180°. In this sense the straight angles were imposed by the pseudosymmetry.

Meanwhile many more silicate crystal structures have been determined, and they are known with much higher precision than could be attained before 1961. Therefore, it seemed worthwhile to have another look at Si—O—Si angles in silicates and SiO_2 polymorphs.

Data

The same data set which had been previously used (Baur, 1978) to arrive at a predictive equation for the Si—O bond length in tetrahedral coordination was taken as a data base. It was augmented by data for a new phase of coesite (Kirfel, Will & Arndt, 1979) which crystallizes in space group $P2_1/a$ and for the Si_2O_7 group in $Si_5O(PO_4)_6$ (Mayer, 1974). In all, data from 109 precisely determined crystal structures were used. The silica polymorphs in the data set besides $P2_1/a$ coesite are synthetic tridymite (Baur, 1977), low quartz (Zachariasen & Plettinger, 1965), low cristobalite (Dollase, 1965) and $C2/c$ coesite (Gibbs, Prewitt & Baldwin, 1977). Not added were the data on terrestrial tridymite (Konnert & Appleman, 1978), even though this structure alone has 160 O atoms in the asymmetric unit. The reason for omitting it is that it was refined with the restrained-parameter structure-factor least-squares method (Konnert, 1976) in which predicted interatomic distances are used as observations along with X-ray diffraction data. The 160 shortest Si—Si distances were restrained to measure 3·08 Å. There is no way of knowing from this refinement what the Si—Si distances would have been without this restraint.

Therefore, only 247 silicate tetrahedra were considered which have a total of 548 individual Si—O—Si angles with a mean experimental standard deviation of a little less than 0·4°. This count is based on the number of Si—O—Si angles originating in each symmetrically separate SiO_4 tetrahedron in the structures which were included in the set of data. According to this count low quartz, for example, contributes four angles to the data set. If instead the number of symmetrically unique O atoms are counted then low quartz contributes only one angle to the set. In this latter case the number of total observations in the set is 293. In Table 1 both counts are listed and it may be seen that the frequency distribution of the angles is not affected by the choice of counting. Of course, these two choices are not the only ones possible. It could be logically argued that we should treat each crystal structure as a unit. If we did that, then low quartz with one unique tetrahedron would have the same weight as synthetic low tridymite with 12 Si atoms in the asymmetric unit. Such counting would effectively reduce the number of points in the data set and has not been used here. In any event, whenever statistics using crystal structure data are presented, it is useful to be explicit about the way the data are counted.

The frequency distribution by Si—O—Si angle in Table 1 in columns 3 and 4 does not take into account the fact that we are dealing here with a three-dimensional distribution. The point has been made by Pedersen (1974) and Kroon & Kanters (1974) in the analogous case of the frequency distribution of O—H···O angles that the representation of such angle data in a simple histogram corresponds to a projection of a three-dimensional distribution into one dimension. In terms of spherical coordinates one can say that angles with different azimuths are all projected into a single meridian. A point close to the zenith (that is to a 180° angle) has only a small solid angle into which it can fall, while a point at low latitude, let us say with a 120° Si—O—Si angle, can fall anywhere on a large area. In order to correct for this and to look at a frequency distribution per unit solid angle the raw counts of columns 3 and 4 must be divided by the sine of the angle (Si—O—Si). The resulting corrected distribution per unit solid angle is given in columns 5

Table 1. *Frequency of occurrence of* Si—O—Si *angles* (°) *in* (*a*) *silicates and* (*b*) SiO_2 *polymorphs when counted by* SiO_4 *tetrahedron and by oxygen atom, before and after correction for unit solid angle*

	Midpoint of range of Si—O—Si	sin (Si—O—Si)	Before correction: number based on		After correction: number based on	
			SiO_4	O	SiO_4	O
(*a*)	117·5	0·8870	3	1	3	1
	122·5	0·8434	4	2	5	2
	127·5	0·7934	24	12	30	15
	132·5	0·7373	68	34	93	46
	137·5	0·6756	138	76	204	112
	142·5	0·6088	102	55	168	90
	147·5	0·5373	48	28	89	52
	152·5	0·4617	24	13	52	28
	157·5	0·3827	26	15	68	39
	162·5	0·3007	11	6	37	20
	167·5	0·2164	4	2	19	9
	172·5	0·1305	2	1	15	8
	177·5	0·0436	14	9	321	206
(*b*)	137·5	0·6756	6	3	9	4
	142·5	0·6088	19	9	31	15
	147·5	0·5373	34	16	63	30
	152·5	0·4617	8	4	17	9
	157·5	0·3827	8	4	21	11
	177·5	0·0436	5	3	115	69

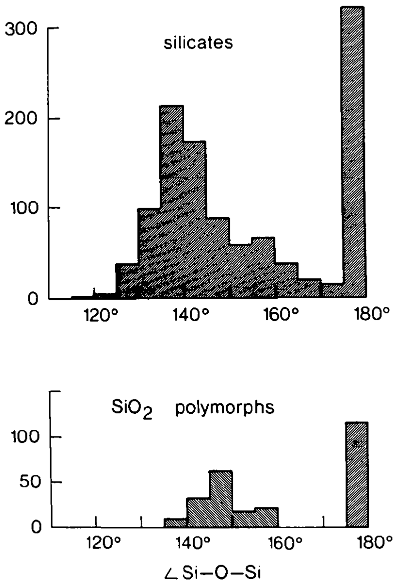

Fig. 1. Histograms of Si–O–Si angles observed in silicates and SiO_2 polymorphs after correction for unit solid angle.

and 6 of Table 1 and in Fig. 1. In the case of the O–H···O angles this correction shifts the maximum from 160 to 180°. The latter value is in agreement with theoretical calculations on the water dimer according to which the minimum energy involves a linear hydrogen bond (Hankins, Moskowitz & Stillinger, 1971).

The configuration of an Si_2O_7 group around a bridging O atom is staggered when the two triangles outlined by the O atoms at opposite ends of the group are rotated by 180° relative to each other. It is eclipsed when both triangles are oriented the same way. A group $O(a)_3Si(a)O(br)Si(b)O(b)_3$ is staggered when the smallest dihedral angle between two planes defined by O(*a*)–Si(*a*)–Si(*b*) and O(*b*)–Si(*b*)–Si(*a*) is 60°. This happens when O(*br*) is located on a site with point symmetry $\bar{3}$. If a mirror plane were passing through O(*br*) normal to the Si(*a*)–Si(*b*) vector this dihedral angle would be 0°. Dihedral angles (or azimuths) defined in this manner were calculated for a selection of the bridging bonds in this sample. The observed dihedral angles range from 0 to 60° and assume all values in between for the silica polymorphs, the zeolites, the paracelsians, the disilicates, the chain silicates (except pyroxenes and amphiboles) and the sheet silicates. Feldspars and some other frameworks display a range of dihedral angles from 0 to 40°. For the pyroxenes and the amphiboles the dihedral angles are usually smaller than 10°, because all the silicate tetrahedra in these structures have one face which is parallel to one plane, namely the plane defined by the octahedral ribbons. Overall it is clear that the bridging bonds have sufficient freedom to assume orientations with different azimuths.

Discussion

The frequency distribution of Si–O–Si angles for the silicates has three maxima: at 139, at 157 and at 180°. The peak at 139° corresponds to the mean Si–O–Si angle of 140° reported by Liebau (1961). This result is affected neither by the way the angles are counted, nor by the trivial geometrical correction by sin (Si–O–Si). The geometrical correction, however, appreciably changes the relative heights of the peaks in the frequency distribution. After the correction the 180° peak is the most prominent, while before it was the lowest. The frequency distribution of the silica polymorphs is similar but one peak is shifted: the maxima are at 147, at 157 and at 180°. Again the peak at 180° is the highest. The difference in the positions of the low-angle peaks for the silicates and for the SiO_2 polymorphs is apparently due to the additional bonding in which the O atoms of the silicates are engaged. Both the average coordination numbers and the average bond-strength sums (Baur, 1970) of the O atoms increase as one moves to narrower Si–O–Si angles. This is the same effect which was observed on a much smaller data base for the disilicates (Baur, 1971).

The frequency distribution observed here for the Si–O–Si angles of the SiO_2 polymorphs is in its detail very different from the distribution found experimentally (Mozzi & Warren, 1969) for vitreous silica. They found a smooth distribution with Si–O–Si angles ranging from 120 to 180°, with a maximum at 144°. While their maximum coincides with the maximum found for the crystalline SiO_2 polymorphs, the range of the angles found here is only from 137 to 180°, and three separate peaks are within this range. It would appear that the crystalline silica polymorphs are not a very good model for vitreous silica.

Averages are not very meaningful when the population has several peaks in its frequency distribution. Nevertheless, it is instructive to compare the mean Si–O–Si angle for silicates based on columns 3 and 4 of Table 1, which is 142°, with the mean angle weighted according to the geometrical correction (that is based on columns 5 and 6). The corrected weighted mean is 154°. The corresponding simple mean for the SiO_2 polymorphs is 149°, while the corrected weighted mean is 162°. This means that the preferred orientation when expressed as frequency per unit solid angle is shifted by 12 to 13° towards a more open Si–O–Si angle.

A total of eight O atoms are involved in straight Si–O–Si angles in situations where they are constrained by the symmetry of the determined space group. These are in coesite (Gibbs, Prewitt & Baldwin, 1977), $Ba_3Si_4Nb_6O_{26}$ (Shannon & Katz, 1970), $Er_2Si_2O_7$ and $Yb_2Si_2O_7$ (Smolin & Shepelev, 1970), $Sc_2Si_2O_7$ (Smolin, Shepelev & Titov, 1973), leifite (Coda, Ungaretti & Giusta, 1974), zunyite

(Louisnathan & Gibbs, 1972) and in $Si_5O(PO_4)_6$ (Mayer, 1974). All these structures are well documented and these O atoms are *not* characterized by high and very anisotropic temperature factors. Indeed, in these eight compounds there are a total of nine O atoms which have higher temperature factors than the bridging O atoms. There are another 20 O atoms which have lower temperature factors than the bridging atoms. There is no reason to suspect falsely attributed high symmetries in any of these cases. However, the case for the possibility of straight Si—O—Si angles is established most clearly by the four structures with essentially straight bonds, where this configuration is not required by symmetry. These angles are 179·9 (8)° in cordierite (Gibbs, 1966), 177·7 (3)° in gillespite (Hazen & Burnham, 1974), 179·1 (6)° in synthetic low tridymite (Baur, 1977) and 177·8 (7)° in $P2_1/a$ coesite (Kirfel, Will & Arndt, 1979). A straight Si—O—Si bond has also been observed in a neutral silicon ether, bis(triphenylsilyl) ether, $C_{36}H_{30}OSi_2$, by Glidewell & Liles (1978). The Si—O distance within the bridging bond is 1·616 (1) Å.

Conclusion

A study of recently determined crystal structures shows that straight and nearly straight Si—O—Si angles are possible for bridging O atoms. In fact, their number is surprisingly large if one considers the frequency of their occurrence per unit solid angle. The corrected frequency distributions of the angles at the bridging O atoms have three peaks at 139, 157 and 180° (with a mean at 154°) for silicates, and at 147, 157 and 180° (with a mean at 162°) for the silica polymorphs. Bonding theories for the silicates and silica must take these facts into account. A theoretical rationale based on CNDO/2 calculations is available for Si—O—Si angles of about 150° (Tossell & Gibbs, 1978). This corresponds most closely to the peak at 147° of the SiO_2 polymorphs. A rationale for the small peaks at 157° and the large peaks at 180° is yet to be found.

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Note added in proof: After this paper was accepted for publication an article bearing upon the present subject matter appeared in print (DeJong & Brown, 1980). These authors calculated among other things the conformations of the $H_6Si_2O_7$ molecule by semi-empirical molecular-orbital theory. Their results cannot be directly compared with the empirical evidence presented here, because for obvious reasons they made calculations for only three conformations of the molecule. However, they point out that the results of their calculations would be consistent with a double minimum in the angle Si—O—Si for vitreous silica, if vitreous silica has a bimodal distribution of the distances Si—O or the dihedral angle. Vukcevich (1972) had suggested such a bimodal Si—O—Si distribution (peaks at 138 and 146°) in order to interpret the thermal expansion, compressibility and specific heat of vitreous silica. DeJong & Brown (1980) also refer to the refinement of Mozzi & Warren's (1969) data by DaSilva, Pinatti, Andersson & Rudee (1975). According to the latter authors the most probable Si—O—Si angle in vitreous silica is at 152° and not at 144° as calculated by Mozzi & Warren. This would place it halfway between the two low-angle peaks identified here for the silica polymorphs. All this means that qualitatively there is a better agreement between the crystalline silica polymorphs and vitreous silica than I had assumed above. The one outstanding difference remains in the peak at 180°.

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$Sc_{44}Os_7$ and $Sc_{44}Ir_7$ with the $Mg_{44}Rh_7$ Structure Type

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Abstract

The $Mg_{44}Rh_7$ structure type with space group $F\bar{4}3m$ and $Z = 8$ is found for $Sc_{44}Os_7$ [$a = 20{\cdot}771$ (5) Å, $D_x = 4{\cdot}906$ (4) Mg m^{-3}, μ(Mo $K\alpha$) = 27·2 mm^{-1}, $F(000) = 11\,648$] and $Sc_{44}Ir_7$ [$a = 20{\cdot}755$ (3) Å, $D_x = 4{\cdot}937$ (2) Mg m^{-3}]. $Sc_{44}Os_7$ positional parameters were refined from single-crystal diffractometer data to a final weighted $R = 0{\cdot}052$. $Sc_{44}Ir_7$ with the same structure was obtained by heat treatment at 1023 K. Its isotypy with $Sc_{44}Os_7$ was recognized from powder photographs. The structure can be described by a packing of nested polyhedra units. Their sequence along the cube diagonal is γ-brass, γ-brass*, α-Mn(–C), Ti_2Ni.

Introduction

No phase diagrams of the Sc-rich part of the Sc–Os or Sc–Ir systems are available in the literature. The only known phases are ScIr with the CsCl structure (Aldred, 1962) and $Sc_{11}Os_4$ ($Sc_{11}Ir_4$) recently reported by Chabot, Cenzual & Parthé (1980*a*). The structure of the latter two compounds is face-centred cubic and closely related to the Th_6Mn_{23} type. In the course of these studies the presence of another cubic phase was oberved, of which the identification and structure form the content of this paper.

Experimental

Alloys were prepared by arc-melting techniques, under an argon atmosphere, from elements of high purity (sublimed Sc 99·95% and 99·9% for transition elements of Group VIII).

A single crystal of 50 μm mean diameter was isolated from a crushed ingot with starting composition equivalent to Sc_6Os. The true composition of this phase was revealed later to be $Sc_{44}Os_7$. The structure is cubic, with a cell parameter $a = 20{\cdot}771$ (5) Å, obtained from the least-squares refinement of 2θ values of 20 reflexions measured with the lattice-parameter-determination program of a Philips PW 1100 diffractometer. According to the Laue group ($m3m$) and the lack of systematic extinctions other than those due to the F Bravais lattice the possible space groups are $F432$, $F\bar{4}3m$ and $Fm3m$. Data collection was carried out on the automatic four-circle diffractometer in the θ–2θ mode with graphite-monochromated Mo $K\alpha$ radiation, up to $\sin\theta/\lambda = 0{\cdot}61$ Å^{-1}, yielding 402 independent reflexions.

A comparison of a Guinier powder pattern of the Sc_6Os crushed melt with a *LAZY PULVERIX* simulated powder pattern (Yvon, Jeitschko & Parthé, 1977), using the point positions of the $Mg_{44}Rh_7$ structure type* (Westin & Edshammar, 1971), suggested that both compounds are probably isotypic. The refinement of the structure was carried out in space group $F\bar{4}3m$, isotypy with $Mg_{44}Rh_7$ being assumed. Scattering factors and anomalous-disperison corrections were taken from *International Tables for X-ray Crystallography* (1974). Intensities were corrected for spherical absorption and structure factors were corrected for isotropic secondary extinction. The structure refinement using the full-matrix least-squares program *CRYLSQ* (XRAY system, 1976) was obtained from 385 reflexions with $|F| > 3\sigma_F$. In a first

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* This structure type was determined independently by Samson & Hansen (1972) on $Na_{44}Tl_7$. For reasons of simplicity they call their phase Na_6Tl.

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