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The oxygen packings of low-quartz and ReO_3 under high pressure

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Abstract. Changes of structures consisting of corner-connected polyhedra under high pressure can be described by changes of the anion packing.

High-pressure structure data of the low-quartz modifications of SiO_2 and GeO_2 were used to calculate the Dirichlet domains of the oxygen anions. The results indicate that the deformation of the oxygen framework causes the changes of the quartz structure under high pressure. The framework becomes similar to the arrangement of a cubic body-centered lattice. With this model the distortion of the SiO_4 and GeO_4 tetrahedra with increasing pressure easily can be understood.

The behaviour of ReO_3 under pressure can be described by the deformation of a sphere packing which is built up by the oxygen anions.

Introduction

Hazen and Finger (1982) developed the polyhedral approach to describe the changes of crystal structures under high pressure, as well as at high temperature, and with variable composition, respectively. They generally characterize the compression or thermal expansion by means of the behaviour of the individual polyhedra. This model is very useful for qualitative prediction of the bulk modulus and thermal expansion. In the case of structures which are built up of corner-connected polyhedra, mainly polyhedral tilting should be responsible for structural changes. The volume of empty voids in the framework is reduced under pressure, and the compressibility of the crystal structure is much larger than that of a single polyhedron. A well known example for a structure consisting of corner-linked polyhedra is the quartz structure.

At room temperature and 1 bar, SiO_2 crystallizes with the low-quartz structure in the trigonal space group $P3_221$ or in the enantiomorphic space group $P3_121$. For the following investigations $P3_221$ is used with the origin of the unit cell according to the International Tables (1983). The lattice parameters are $a = 4.9134$ Å and $c = 5.4052$ Å. The oxygen anions occupy the position 6(c) x,y,z, with $x = 0.4141(2)$, $y = 0.2681(2)$ and $z = 0.7855(1)$. The Si^{4+} cations lie on position 3(a) $x,0,2/3$ with $x = 0.46987(9)$ (Le Page and Donnay, 1976).

An isomorphous modification of GeO_2, which is metastable at room temperature has lattice parameters of $a = 4.9845$ Å and $c = 5.6477$ Å. The positional parameters are $x = 0.3965(3)$, $y = 0.3022(4)$ and $z = 0.7578(3)$ for the oxygen ions and $x = 0.45130(6)$ for the Ge^{4+} ions (Glinnemann et al., 1989). The oxygen ions form tetrahedra which are centered by Si^{4+} or Ge^{4+} ions.

The effect of pressure on the low-quartz structure of SiO_2 has been already studied several times. There exists one crystal structure refinement using neutron-powder diffraction data (Jorgensen, 1978) whereas three single-crystal X-ray diffraction measurements are reported (d'Amour et al., 1979; Levien et al., 1980; Glinnemann, 1987). Two high-pressure refinements of the structure of the trigonal GeO_2 modification are published. Jorgensen (1978) performed neutron-powder diffraction measurements up to 2.21 GPa and Glinnemann et al. (1989) reported single crystal investigations with X-rays up to 5.57 GPa.

It has been stated by Levien et al. (1980) that the metastable low-quartz modification of GeO_2 is a high pressure model for SiO_2. In fact, the structure of SiO_2 at 10.2 GPa is similar to that of GeO_2 at ambient conditions. Table 1 shows the most important changes of the low-quartz structure under high pressure. With increasing pressure the c/a axial ratio increases, the SiO_4 and GeO_4 tetrahedra become more and more distorted, and the (Si,Ge)−O−(Si,Ge) angles decrease. In addition, some intertetrahedral oxygen distances are shortened very clearly.

The quartz structure consists of corner-connected tetrahedra, which show cooperative rotation under pressure. The tilt angle δ which describes the tilting of the tetrahedra around the twofold axes (Grimm and Dorner, 1975) in SiO_2 goes from 16.1° at 1 bar to 26.2° at 10.2 GPa. The latter value is similar to that in GeO_2 at 1 bar with $\delta = 26.5°$, which changes to 30.6° at 5.57 GPa (Glinnemann et al., 1989).

The high compressibility of quartz can be explained with the help of the model of polyhedral tilting (Hazen and Finger, 1982). However, it cannot explain the increasing distortion of the tetrahedra with increasing pressure.

The previous authors working on quartz structures (d'Amour et al., 1979; Levien et al., 1980; Glinnemann et al., 1989) suggest that there are two different mechanisms of compression. The changes of the crystal

Table 1. The characteristic changes of the low-quartz structure under high pressure.

P/GPa	c/a ratio	<(O−T*−O)		<(T*−O−T*)
		min	max	
SiO_2				
0.0001[a]	1.1001	108.70(4)	110.39(4)	143.68(9)
2.07[b]	1.1050	108.15(4)	110.7(1)	139.9(2)
3.76[b]	1.1105	107.67(5)	111.3(1)	137.2(2)
4.00[c]	1.1107	107.6(2)	111.1(2)	137.1(4)
4.86[b]	1.1138	107.31(5)	111.6(1)	135.8(2)
5.58[b]	1.1154	107.22(4)	111.8(1)	135.1(1)
6.14[b]	1.1178	106.97(5)	112.2(1)	134.2(1)
7.20[c]	1.1221	106.80(6)	112.49(6)	133.1(1)
10.20[c]	1.1310	106.20(5)	113.72(5)	130.3(1)
GeO_2[a]				
0.0001	1.1331	106.28(7)	113.24(6)	130.0(1)
1.07	1.1405	105.7(1)	113.72(9)	128.4(2)
2.18	1.1484	105.3(1)	114.5(1)	126.7(2)
3.74	1.1577	104.6(2)	115.0(1)	125.0(3)
4.53	1.1620	104.2(2)	115.4(1)	124.4(3)
5.12	1.1652	104.1(1)	116.0(1)	124.1(3)
5.57	1.1679	103.5(2)	116.2(1)	123.3(3)

* T = Si, Ge.
[a] Le Page and Donnay (1976).
[b] Levien et al. (1980).
[c] Glinnemann (1987).
[d] Glinnemann et al. (1989)

structure of SiO_2 at lower pressures can be described in such a way that tilting of the SiO_4 tetrahedra is predominant. At higher pressures and for GeO_2 the compression is supposed to result from the distortion of the tetrahedra, while tilting is negligible.

Another example, that will be described here, is ReO_3. At ambient conditions it crystallizes in the cubic space group $Pm\bar{3}m$ with lattice constant $a = 3.7504(1)$ Å. The oxygen anions occupy the position 3(c) 0,1/2,1/2, the rhenium cations the position 1(b) 1/2,1/2,1/2 (Jørgensen et al., 1986). The structure consists of corner-linked ideal ReO_6 octahedra as in a non-distorted perovskite structure. There exist two structural investigations at high pressures. Jørgensen et al. (1986) performed neutron-powder diffraction measurements up to 2.740 GPa, and Schirber et al. (1984) determined the structure of a single crystal at 1.5 GPa. The time-of-flight Laue method was used to collect these neutron-diffraction data. A phase transition takes place at 0.52 GPa leading to space group $P4/mbm$. This structure can also be refined in space group $Im\bar{3}$ but R-value tests favour the tetragonal model. At slightly higher pressures (0.53 GPa) a cubic structure with space group $Im\bar{3}$ occurs. For ReO_3 the model of polyhedral tilting is also used. The tilt angle ϕ is determined by the relation:

$$\cos\phi = \frac{z+y}{2(z^2+y^2-zy)^{1/2}}$$

y,z are the coordinates of the oxygen anion. It changes from 0° at 1 bar to 14° at 2.740 GPa. The octahedra remain nearly undistorted (Jørgensen et al., 1986).

Quartz structure

The first intention of this work was to find the empty voids in the quartz structure and to study their behaviour with increasing pressure. For this purpose the Dirichlet domains of the oxygen anions were calculated (using only oxygen neighbours) to get the centres of all voids existing in the framework (Koch, 1984). For the calculations the program DIDO (Fischer and Koch, 1984) was used.

In the course of the investigations it became obvious, that the shape of the Dirichlet domains changes when pressure is applied (Fig. 1 a – c). It can be clearly seen that with increasing pressure the Dirichlet domains change their shape in the direction of a distorted cuboctahedron. The Dirichlet domain of SiO_2 at 10.2 GPa and GeO_2 at ambient conditions are nearly identical, verifying that GeO_2 is a high pressure model of SiO_2. An ideal cuboctahedron is the Dirichlet domain of a cubic body-centered lattice. This fact indicates that the packing of the oxygen ions changes with increasing pressure.

The oxygen positions of the SiO_2 and GeO_2 structures at high pressure tend to approach $x = 1/3$, $y = 1/3$, $z = 0.75$ (Fig. 2). If, at the same time, the c/a ratio adopts a value of $\sqrt{3}/\sqrt{2} \approx 1.2247$, the arrangement of the oxygen ions corresponds to a body-centered lattice with cubic metric. Fig. 1 d shows the appropriate Dirichlet domain.

Looking at the O – O distances (Fig. 3), the assumption of the change of the packing is confirmed. SiO_2 and GeO_2 cannot be compared directly, because of the different sizes of the Si^{4+} and Ge^{4+} ions. Therefore it is necessary to standardize both structures. This may be done by calculating normalized O – O distances with lattice constants $a = 1$ Å and c equal to the axial ratio.

In Figures 3 and 4 only high pressure data of Levien et al. (1980) and Glinnemann et al. (1989) are included, because these data are much more precise than the former measurements.

Figure 3 shows the dependence of the O – O distances in SiO_2 and GeO_2 of the c/a ratio which is a measure for pressure. In addition, the values

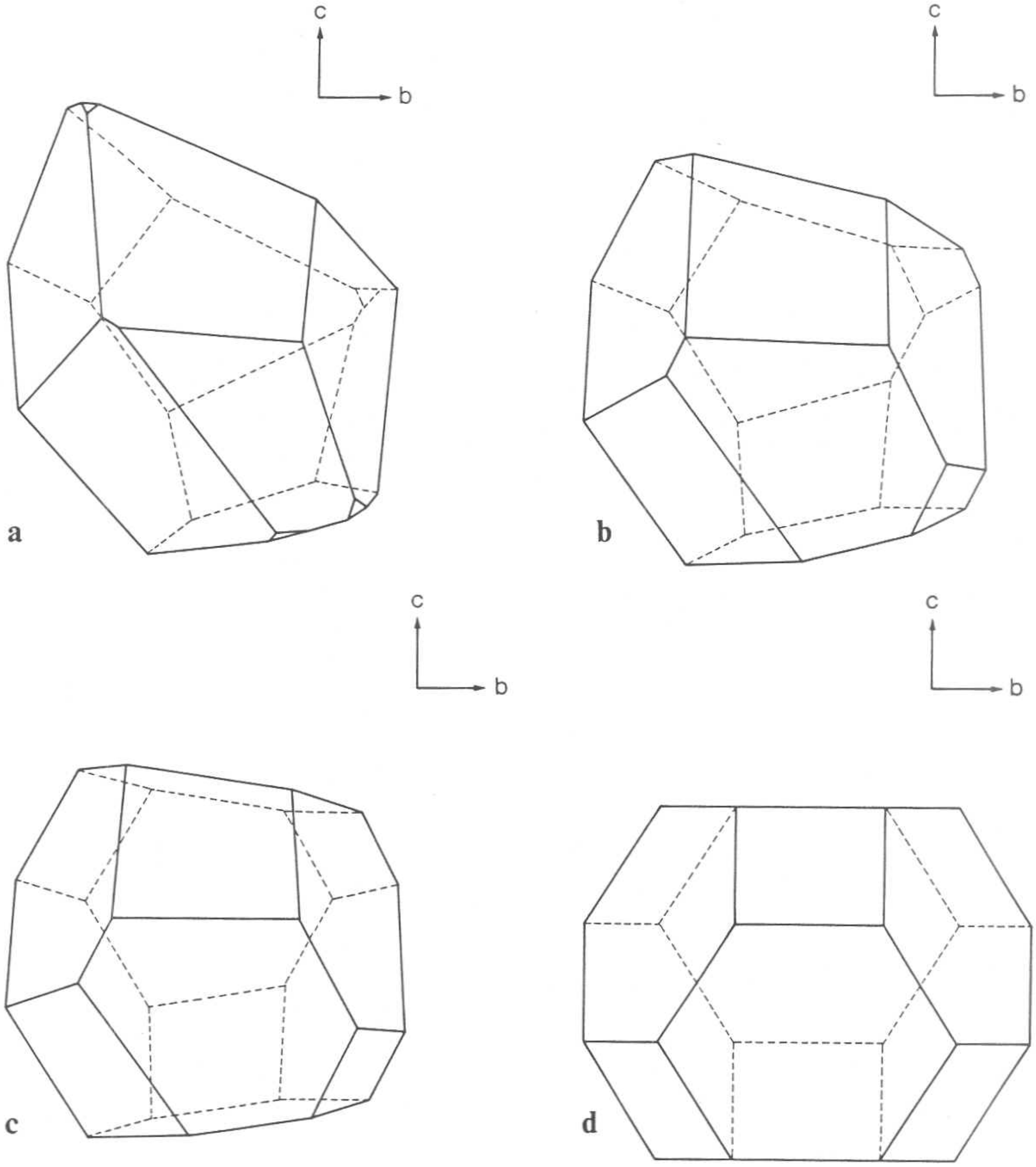

Fig. 1. Dirichlet domains of the oxygen anions in the quartz structure. (a) SiO_2 at ambient conditions, (b) SiO_2 at 10.2 GPa or GeO_2 at ambient conditions, (c) GeO_2 at 5.57 GPa, (d) cubic *I* framework.

for high-quartz are given for comparison (Wright and Lehmann, 1981). Unfortunately the sphere packings in space group $P3_221$ or $P3_121$ have not been derived yet. From Figure 3 it can be concluded that at low pressure the oxygen arrangement nearly corresponds to a sphere packing with six contacts per sphere as to be expected for corner-connected tetrahedra. It is obvious that with increasing c/a ratio the coordination number increases. At 5.57 GPa the oxygen anions have nine nearest neighbours in GeO_2,

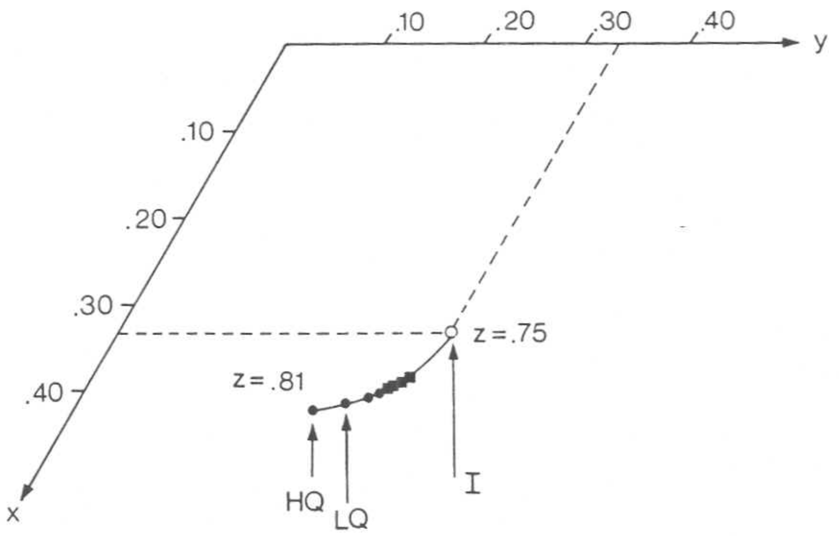

Fig. 2. Oxygen positions in the quartz structures of SiO_2 and GeO_2 with increasing pressure. The position for a cubic *I* framework is also given. HQ = high-quartz, LQ = SiO_2 at ambient conditions. ● = SiO_2, ■ = GeO_2.

although the O–O distances are not of the same length. At $c/a = \sqrt{3}/\sqrt{2}$ the distances in a cubic *I* lattice are marked. Extending the connecting lines between the measured points it can be assumed that these values could be reached at higher pressures. But the symmetry $P3_221$ of the quartz structure would be preserved, caused by the trigonal arrangement of the cations.

With such a model the increasing distortions of the SiO_4 and GeO_4 tetrahedra can easily be explained. A cubic body-centered framework contains only one kind of voids. These are flattened tetrahedra. Their centres build up a *W** configuration (Hellner et al., 1981). As shown in Figure 4 the tetrahedral voids in the quartz structure become more and more flattened when the packing of the oxygen ions changes towards an *I* framework. In the case of GeO_2 one of the (O–Ge–O) angles which should decrease with increasing pressure increases above 4.0 GPa. This may be caused by the size of the Ge^{4+} ion. If it is assumed that the oxygen ions are in contact with each other, the Ge^{4+} ion is too large for fitting the tetrahedral voids. At 5.57 GPa the structure has two different Ge–O distances (Glinnemann et al., 1989). It is presumed that the Si^{4+} and Ge^{4+} ions do not tolerate a strongly distorted coordination tetrahedron as occurs in an *I* framework. Probably a phase transition takes place before such a framework is realized.

ReO_3 structure

A further example will demonstrate that structural changes which are described by polyhedral tilting in the model of Hazen and Finger (1982), may be interpreted by changes of the anion framework.

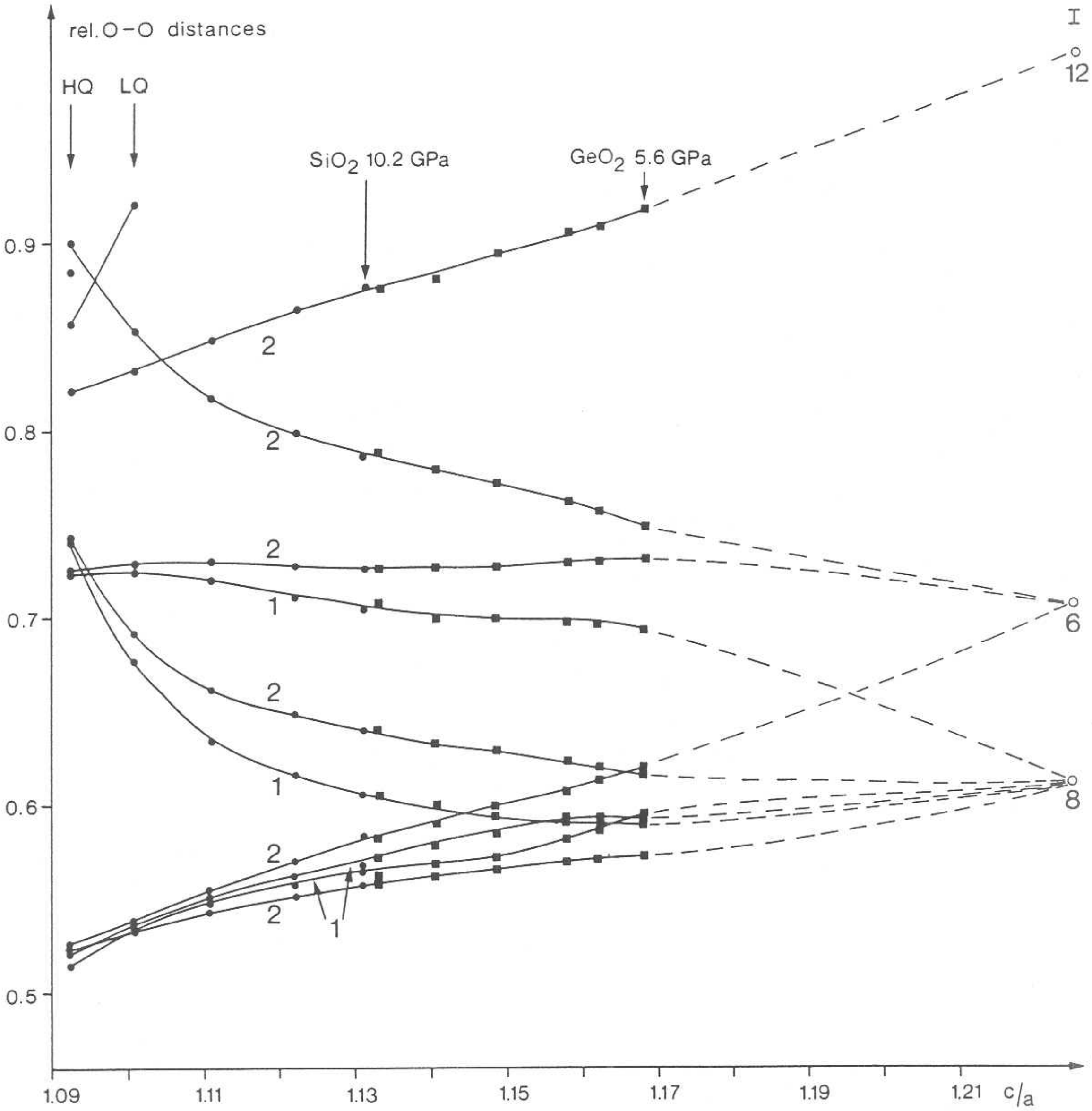

Fig. 3. Relative O – O distances in the quartz structure versus c/a ratio. The number of distances is also given. HQ = high-quartz, LQ = SiO_2 at 0.0001 GPa, I = I lattice, ● = SiO_2, ■ = GeO_2. The lines are connecting lines between the measured points, not calculated.

The structural changes with pressure of ReO_3 can be described by means of sphere packings. For all cubic space groups the sphere packing conditions have been published (Fischer, 1973, 1974).

ReO_3 crystallizes at ambient conditions in the space group $Pm\bar{3}m$. The oxygen anions build up a configuration belonging to the invariant lattice complex J (International Tables, 1983). This arrangement corresponds to a sphere packing with eight contacts per sphere. The appropriate symbol is $8/3/c2$ (Fischer, 1973). Such a framework contains ideal octahedral voids, occupied by Re^{6+} ions and cuboctahedral voids which are empty in ReO_3 (Hellner et al., 1981). Above 0.53 GPa a phase transition takes place to

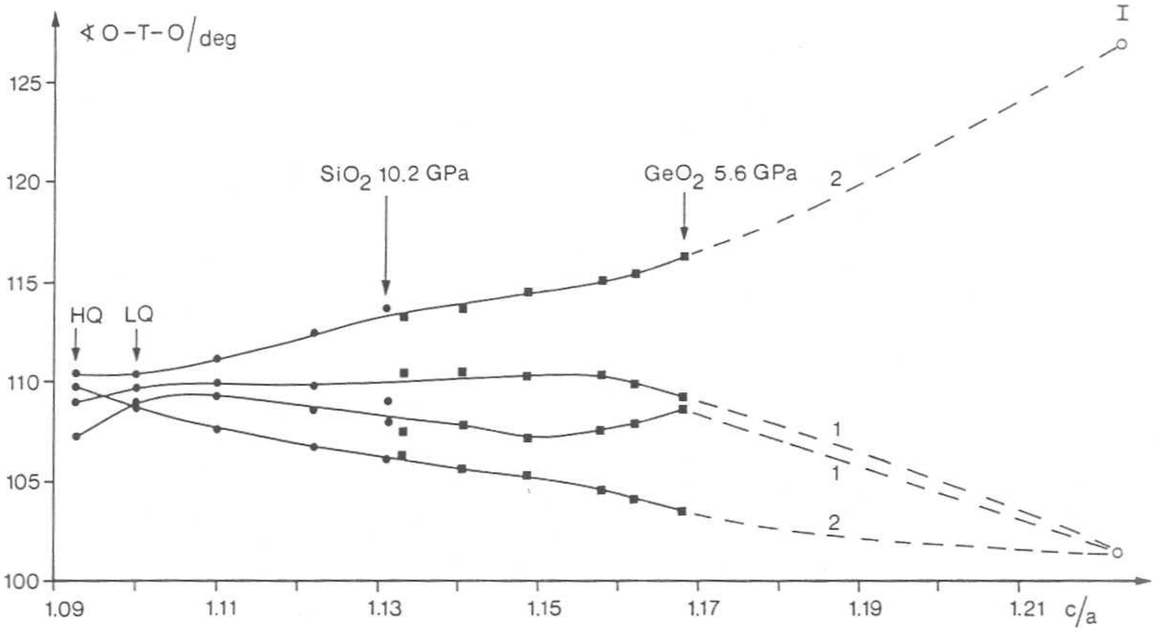

Fig. 4. Calculated (O–T–O) angles of ideally centered tetrahedra versus c/a ratio. The number of angles per tetrahedron is also given. T = Si,Ge, HQ = high-quartz, LQ = SiO_2 at 0.0001 GPa, I = I lattice, ● = SiO_2, ■ = GeO_2. The lines are connecting lines, not calculated.

Table 2. Positional parameters of oxygen ions in ReO_3 depending on pressure and deviation from the parameter restriction for the sphere packing of type $8/3/c2$ in $Im\bar{3}$.

P/GPa	y_{obs}	z_{obs}	z_{calc}
0.0001	0.25	0.25	0.25
0.73	0.265(2)	0.232(1)	0.234
1.285	0.273(1)	0.225(1)	0.225
1.725	0.2763(9)	0.2197(8)	0.221
2.270	0.280(1)	0.2158(9)	0.216
2.740	0.281(1)	0.2104(9)	0.215

space group $Im\bar{3}$ which is a subgroup of $Pm\bar{3}m$ with double lattice constant a. In $Im\bar{3}$ the J configuration occurs as limiting form in position 24(g) 0,y,z with $y = 0.25$ and $z = 0.25$ (Koch, 1974).

The condition for a sphere packing of type $8/3/c2$ is

$$16yz - 8y - 8z + 3 = 0.$$

During the deformation of the oxygen framework this sphere packing condition may be maintained.

In ReO_3 this equation is fulfilled very well, as shown in Table 2. Jørgensen et al. (1986) give parameters 0,y,z for the oxygen ions with $y < z$. This point configuration is congruent to a second one with $y > z$ (Fischer and Koch, 1983). For the following considerations parameters with $y > z$ are used.

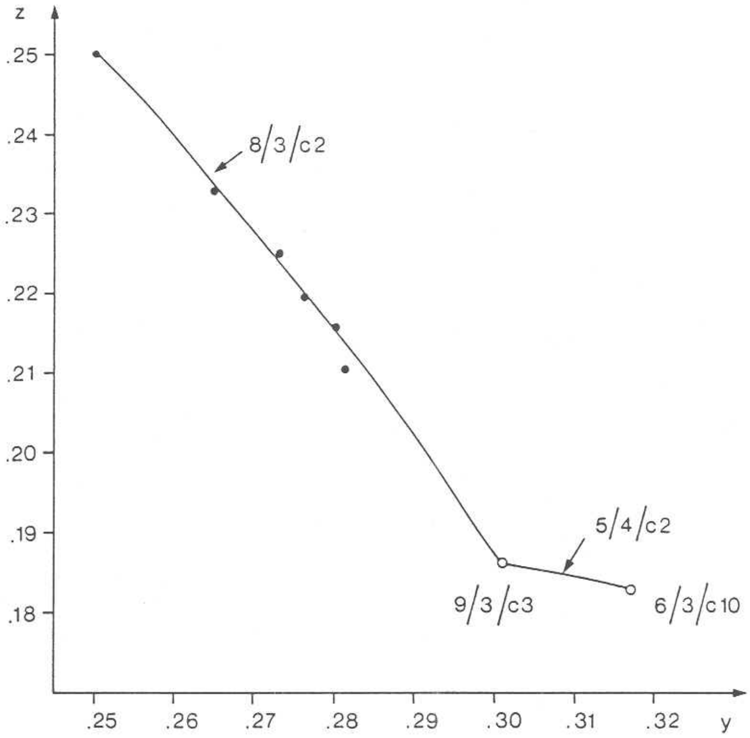

Fig. 5. Possible sphere packings for position 24(*g*) 0*yz* in $Im\bar{3}$ (Fischer, 1973). Full circles = oxygen parameters of ReO_3 (Jørgensen et al., 1986).

Figure 5 illustrates the regions of existence of sphere packings for the position 24(*g*) 0,*y*,*z* in space group $Im\bar{3}$. The oxygen positions at different pressures are marked with full circles.

At positional parameters of $y = 0.3010$ and $z = 0.1860$ an additional shortest distance occurs, and the corresponding sphere packing is 9/3/*c*3 (Fischer, 1973). The framework symbol for this arrangement is *I*[12*i*] (Hellner et al., 1981). One further neighbour with a slightly larger distance exists, so that the coordination number of the framework atoms may be regarded as ten. This can be seen in Figure 6. The distances in an ideal sphere packing of type 8/3/*c*2 in the parameter range between a *J* and an *I*[12*i*] framework are given. They refer to a lattice constant of $a = 1$ Å. Full circles show the O–O distances in ReO_3 under pressure. During the deformation the ideal octahedral voids are maintained, while 25% of the cuboctahedral voids are distorted to ideal icosahedral voids. The rest splits up into trigonal prisms and voids of pyramidal shape (Hellner et al., 1981). As shown by Hellner et al. (1981) there exist some crystal structures with an *I*[12*i*] framework, whereas the cation arrangement is analogous to that of perovskite. These are, for example, the structures of $CaCu_3Mn_4O_{12}$ and $NaMn_7O_{12}$. In other structures like $Cu_3Ta_2Ti_2O_{12}$ and $CuTa_2O_6$ showing the same framework only part of these voids are occupied.

It is therefore assumed that by further increasement of pressure the oxygen arrangement of ReO_3 could form an *I*[12*i*] framework. The estimated pressure is about 10 GPa.

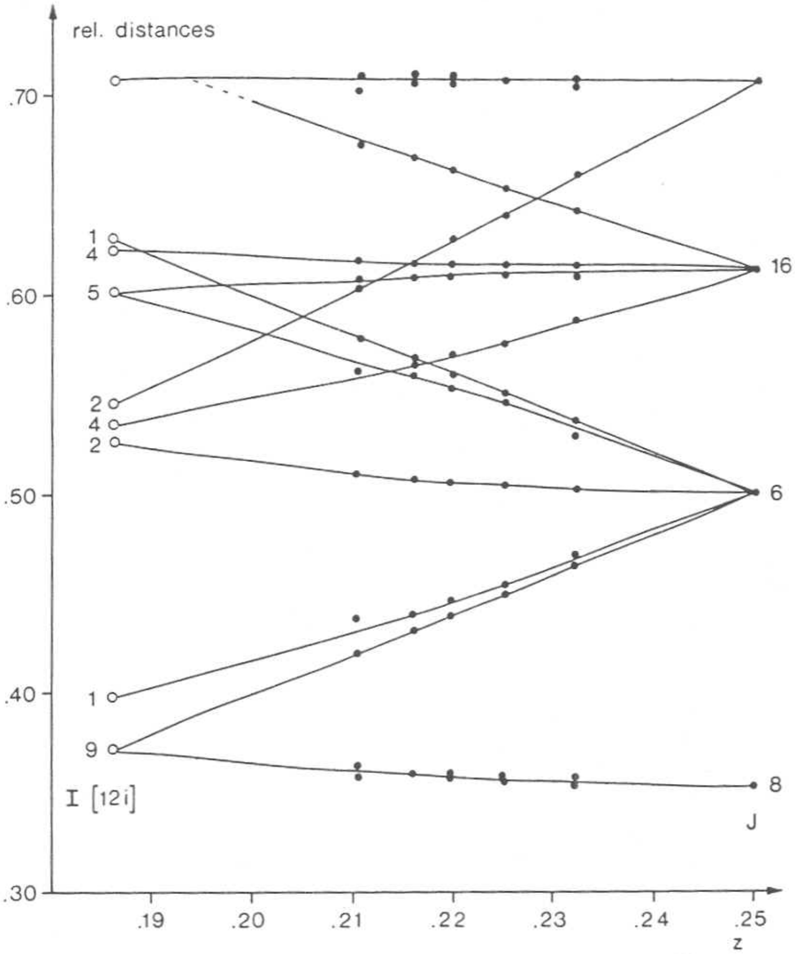

Fig. 6. Distances in an ideal sphere packing of type 8/3/*c*2 in $Im\bar{3}$ refering to a lattice constant of $a = 1$ Å. The number of distances is also given. Full circles = corresponding O–O distances in ReO_3 (Jørgensen et al., 1986).

Discussion

As shown in this work, it is useful to look not only at the polyhedra but also to the anion packing for understanding the high pressure behaviour of structures consisting of corner-connected polyhedra. Helpful tools to indicate such changes are the knowledge of sphere packings and the calculation of Dirichlet domains. But only for the cubic space groups are all conceivable sphere packings available (Fischer, 1973, 1974). All types of homogenous tetragonal sphere packings have been derived (Fischer 1970, 1971), but only a very few examples have been published. Calculations of the Dirichlet domains can be done very easily with the program DIDO (Fischer and Koch, 1984). Regarding these polyhedra as well as considering the anion–anion distances (also given by DIDO) may lead to the recognition of changes of the anion packing.

In the case of the quartz structure the increasing distortions of the SiO_4 and GeO_4 tetrahedra can be explained by changing the oxygen packing towards a cubic *I* framework, whereas it is not possible to explain these distortions with the model of polyhedral tilting. The high pressure behaviour of ReO_3 may be characterized by deformation of a sphere packing as well as by polyhedral tilting. Both models predict undistorted ReO_6 octahedra. Moreover the sphere packing model suggests that at higher pressures the oxygen anions may form an $I[12i]$ framework. This should be proved experimentally in the future. The sphere packing model is a geometric model and does not allow an explanation for the slightly different cation–anion distances in the quartz structure or the distortions of the ReO_6 octahedra in the ReO_3 structure. These deviations are caused by repulsion and bonding forces between the ions.

It is also not possible to elucidate the phase transition in ReO_3 at 0.52 GPa resulting in space group $P4/mbm$. In this case the oxygen anions occupy two different positions and therefore do not form a homogeneous sphere packing. The rotation of the octahedra in $P4/mbm$ may lead to a packing in which one kind of oxygen ions has eight and the other nine neighbours. Such an arrangement would have a lower density than an $I[12i]$ framework. Therefore it is supposed that the structure with symmetry $Im\overline{3}$ is stable at higher pressures.

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