

THE STRUCTURE OF ZIRCON: A COMPARISON
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ABSTRACT

An anisotropic refinement of a non-metamict zircon [$a=6.607(1)$, $c=5.982(1)$ Å; $I4_1/amd$; $Z=4$, $\rho=4.714$ gm/cc; $R=0.019$] from Kragero, Norway, produced these positional parameters for oxygen: $y=.0661(1)$; $z=.1953(1)$. The principal structural unit is a chain of alternating edge-sharing SiO_4 tetrahedra and ZrO_8 triangular dodecahedra extending parallel to c . The chains are joined laterally by edge-sharing ZrO_8 dodecahedra and are responsible for zircon's prismatic habit and cleavage, its extreme birefringence and optically positive character. Similar chains occur in garnet extending in three mutually perpendicular directions, but they are cross-linked by YO_6 octahedra as well as by XO_8 dodecahedra.

Oxygen in zircon is coordinated by one Si at 1.622(1) Å and two Zr at 2.131 and 2.268 Å. The mean bond angle at oxygen is 120° , suggesting that its orbitals are sp^2 hybridized, leaving a lone pair available to form a double bond with Si. In garnet oxygen is four-coordinated and the mean bond angle is $\approx 108^\circ$, suggesting sp^3 hybridization with no lone pairs available for double bonding. This may explain why the Si-O bond in garnet is ≈ 0.02 Å longer than in zircon.

As in garnet, the SiO_4 group is a tetragonal bisphenoid elongated parallel to c , and the Si vibration ellipsoid is prolate in the same direction. Zr vibrates isotropically, but oxygen has its maximum vibration axis normal to the plane of the coordinating Si and Zr atoms. The distortions of the ZrO_8 triangular dodecahedron from an ideal hardsphere model can be rationalized in terms of cation-cation repulsion across its shared edges.

INTRODUCTION

Zircon, ZrSiO_4 , occurs as an accessory mineral in granitic and syenitic igneous rocks and is a common detrital component of sedimentary rocks. Its relatively high density and resistance to weathering have contributed to its extensive use in heavy mineral studies.

The crystal structure of zircon was determined independently by Vegard (1926), Binks (1926), Hassel (1926), and Wyckoff and Hendricks (1927). Krstanović (1958) has since refined the structure using two-dimensional methods and obtained an Si-O bond length of 1.612 Å. White and Gibbs (1967) observed that this bond length was inconsistent with the $\text{SiK}\beta$ wave-length shift measured for twelve minerals with only Si in tetrahedral coordination. This discrepancy led to the present three-dimensional refinement, which yielded an Si-O bond length of 1.622 Å in better agreement with the value predicted by White and Gibbs. During the course of our study, Krstanović, Djurić, and Ilić (1968) reported refined oxygen coordinates [$x=0.064(1)$; $z=0.194(1)$] for a metamict and

a non-metamict zircon using three-dimensional data but they did not give cell dimensions or bond lengths for either structure.

EXPERIMENTAL DETAILS

The zircon crystal used in this study was obtained from a syenite in Kragero, Norway. Sharp diffraction maxima on Weissenberg photographs indicate that this specimen is non-metamict. This is substantiated by the fact that the cell dimensions agree with those given by Holland and Gottfried (1955) for gem-quality, unirradiated zircon. Electron microprobe analysis indicated that the only impurity present in detectable amounts is hafnium (~ 1 wt. percent). The unit cell parameters are $a = 6.607(1)$; $c = 5.982(1)$ Å, $Z = 4$, $\rho = 4.714$ gm/cc. The space group is $I4_1/amd$. More than 550 non-zero intensities were measured with an equi-inclination Weissenberg single-crystal diffractometer using Nb-filtered Mo radiation and a scintillation counter. The intensities were recorded on a stripchart, integrated with a planimeter, corrected for Lp and absorption effects and converted to structural amplitudes. These were submitted to an isotropic least-squares calculation (Busing, Martin, and Levy, 1962) using the positional parameters for oxygen (0.0, 0.067, 0.198) determined by Krstanović (1958), where the origin was chosen at $2/m$. Form factors were taken from the International Tables, Vol. III for Si and O, that for Zr^{4+} was taken from Cromer and Waber (1965) and corrected for the real part of anomalous dispersion. The $|F_{obs}|$'s were weighted according to a scheme proposed by Hanson (1965), and the weights were adjusted to give approximately equal $\langle w\Delta F^2 \rangle$ for ten equally populated groups of increasing $|F_{obs}|$'s thereby making $\langle w\Delta F^2 \rangle$ essentially independent of magnitude of the individual $|F_{obs}|$'s.

A relatively large number of low angle, high intensity reflections were rejected in the final refinement because of extinction effects, and the unweighted residual for 498 $|F_{obs}|$'s was 0.020 (weighted $R = 0.024$). The anisotropic refinement reduced R to 0.019 (weighted $R = 0.022$), and an R -factor test (Hamilton, 1965) showed that this refinement was more significant than the isotropic one.

The final positional and thermal parameters are given in Tables 1 and 3. The interatomic distances and bond angles are listed in Table 2.

DISCUSSION

The principal structural unit in zircon is a chain of alternating edge-sharing SiO_4 tetrahedra and ZrO_8 triangular dodecahedra extending parallel to c (Fig. 1). The chains are joined laterally by edge-sharing

TABLE 1. POSITIONAL PARAMETERS, ANISOTROPIC TEMPERATURE FACTORS, AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS FOR ZIRCON

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B (equiv.)
Zr	0.0	0.75	0.125	0.00096(8) ^a	0.00096(8)	0.0012(1)	0.0	0.0	0.0	0.23(1)
Si	0.0	0.75	0.625	0.0014(1)	0.0014(1)	0.0027(3)	0.0	0.0	0.0	0.45(2)
O	0.0	0.0661(1)	0.1953(1)	0.0037(2)	0.0031(2)	0.0029(2)	0.0	0.0	-0.0000(2)	0.53(2)

^a Estimated standard deviations are in parentheses and refer to the last decimal place.

TABLE 2. INTERATOMIC DISTANCES (Å) AND ANGLES (DEGREES) IN ZIRCON

<i>SiO₄ Tetrahedron</i>			
Si-O	[4] ^a		1.622 (1) ^b
<i>O-O Distances</i>			<i>Angles at Si</i>
O-O	[2]	2.430 (2) ^c	97.0 (1)
O-O	[4]	2.752 (2)	116.06 (8)
Mean 2.645			109.71
<i>ZrO₈ Triangular Dodecahedron</i>			
Zr-O(A)	[4]		2.268 (1)
Zr-O(B)	[4]		2.131 (1)
Mean			2.200
<i>O-O Distances</i>			<i>Angles at Zr</i>
O(A)-O(A')	[2]	2.430 (2) ^c	64.8 (1)
O(A)-(B)	[8]	2.842 (1)	80.41 (2)
O(A)-O(B')	[4]	2.494 (2) ^d	69.00 (5)
O(B)-O(B')	[4]	3.071 (2)	92.23 (1)
Mean 2.770			78.77
<i>Cation-Cation Distances</i>			<i>Angles at oxygen</i>
Zr-Zr'		3.626 (2)	111.02 (5)
Zr-Si		2.991 (2)	99.17 (6)
Zr'-Si		3.626 (2)	149.81 (5)

[^a] Multiplicity.

(^b) Estimated standard deviations refer to the last decimal place.

^c Edge shared between tetrahedron and dodecahedron.

^d Edge shared between two dodecahedra.

TABLE 3. MAGNITUDE AND ORIENTATIONS OF PRINCIPAL AXES OF THE THERMAL ELLIPSOIDS

Atom Axis	rms displacement Å	Angle (°) with respect to:		
		<i>a</i> ₁	<i>a</i> ₂	<i>c</i>
Si <i>r</i> ₁	0.055 (5) ^a	0	90	90
<i>r</i> ₂	0.055 (6)	0	90	90
<i>r</i> ₃	0.070 (4)	90	90	0 (3.4)
O <i>r</i> ₁	0.072 (3)	90	91.4 (13.7)	1.4 (13.6)
<i>r</i> ₂	0.083 (3)	90	1.4 (13.7)	88.6 (13.7)
<i>r</i> ₃	0.092 (3)	0	90	90

^a Estimated standard deviations are in parentheses.

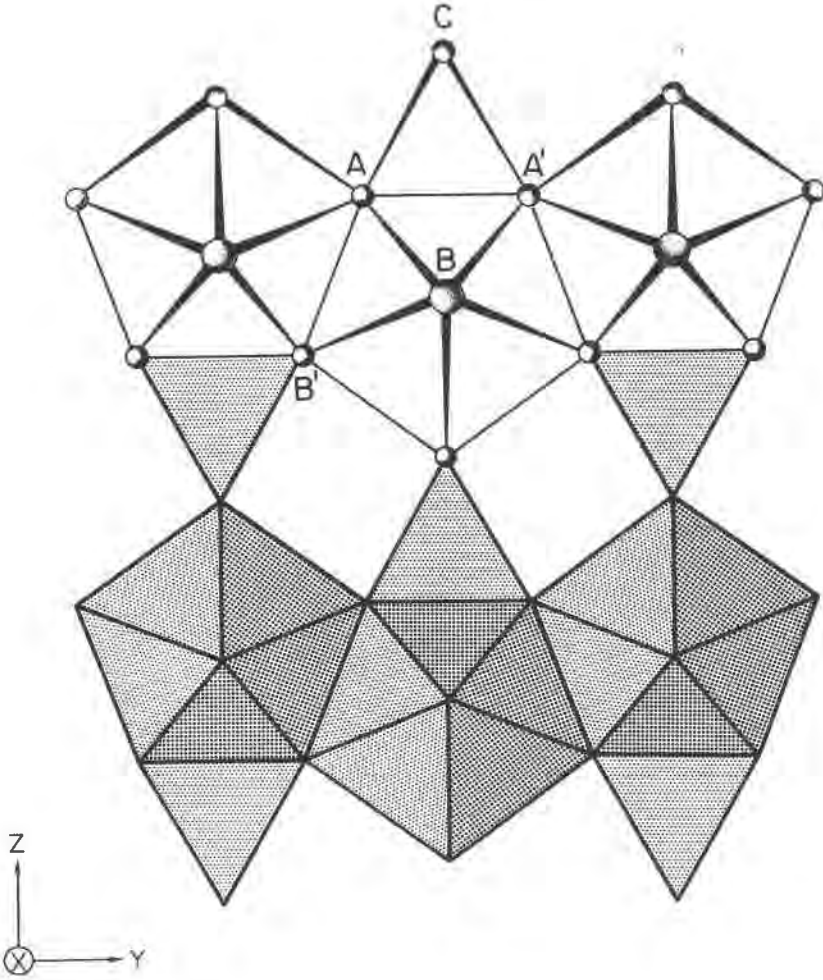


FIG. 1. The chains of alternating edge-sharing SiO_4 tetrahedra and ZrO_8 triangular dodecahedra extending parallel to c and joined laterally by edge-sharing dodecahedra.

dodecahedra (*cf.* Figs. 1 and 2) and are responsible for zircon's prismatic habit and (110) cleavage, its extreme birefringence and optically positive character.

Similar chains occur in garnet (Fig. 3), extending in three mutually perpendicular directions, but they are cross-linked by YO_6 octahedra as well as by XO_8 dodecahedra. In zircon octahedral voids are present but contain no cations. The structural similarities of zircon and garnet account for their similar hardness, density and high refractive indices.

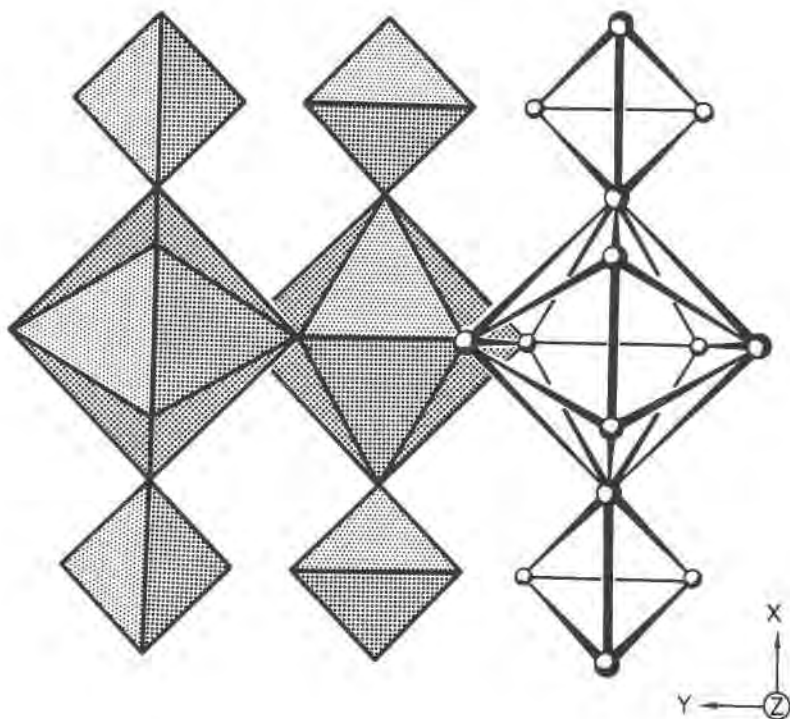


FIG. 2. The chains of alternating edge-sharing SiO_4 tetrahedra and ZrO_8 dodecahedra projected on (001) and showing the edgesharing between dodecahedra.

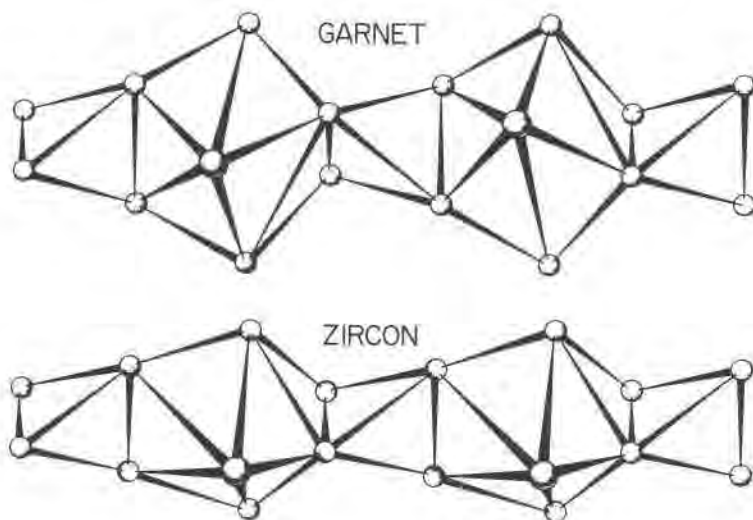


FIG. 3. A comparison of the alternating edge-sharing tetrahedra and dodecahedra chains in zircon with similar chains in garnet.

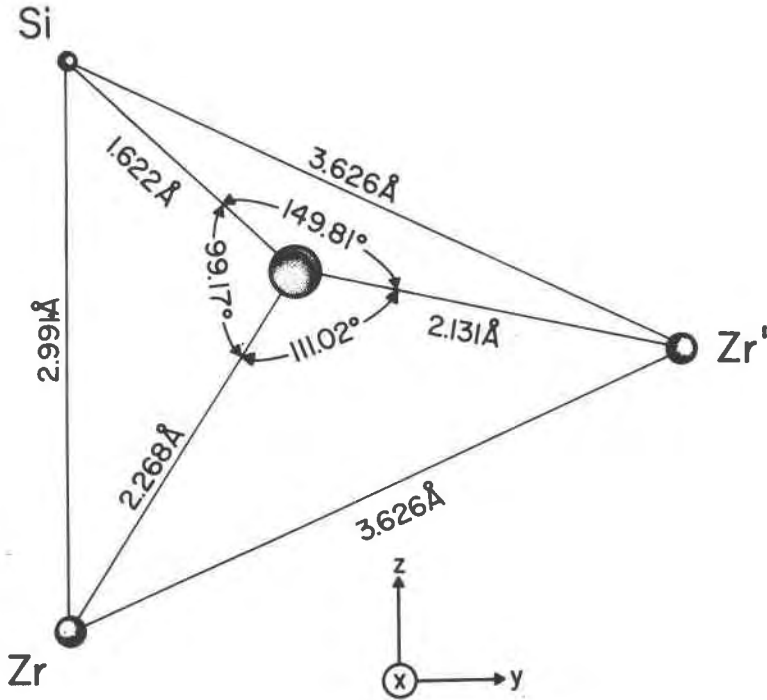


FIG. 4. The coordination, interatomic distances and angles for oxygen.

Oxygen coordination and the Si-O bond. The oxygen in zircon is coordinated in a planar array by one Si at 1.622 Å and two Zr at 2.131 and 2.268 Å (Fig. 4), and it has its maximum vibration axis normal to this plane (Table 3). The length of the Si-O bond is similar to the predicted value of 1.624 Å for a three-coordinated oxygen (Brown and Gibbs, 1969). The mean bond angle at oxygen is 120° , suggesting that its orbitals are sp^2 hybridized, leaving a lone pair perpendicular to the planar array available to form a double bond with Si. In garnet oxygen is four-coordinated by one Si, two $\{X^{2+}\}$ cations and one $[Y^{3+}]$ cation, suggesting sp^3 hybridization of the oxygen orbitals, with no lone pairs available for double bonding (Griffith, 1969). This may explain why the Si-O bond in garnet (Novak and Gibbs, 1971) is 0.01–0.03 Å longer than in zircon, but fails to explain the long Si-O bond of 1.641 Å in topaz (Ribbe and Gibbs, 1971) where oxygen is three-coordinated by two Al and one Si.

Cation coordination polyhedra. The SiO_4 group in garnet has site symmetry $\bar{4} \equiv S_4$ and in zircon $\bar{4}2m \equiv D_{2d}$, but both are tetragonal disphenoids

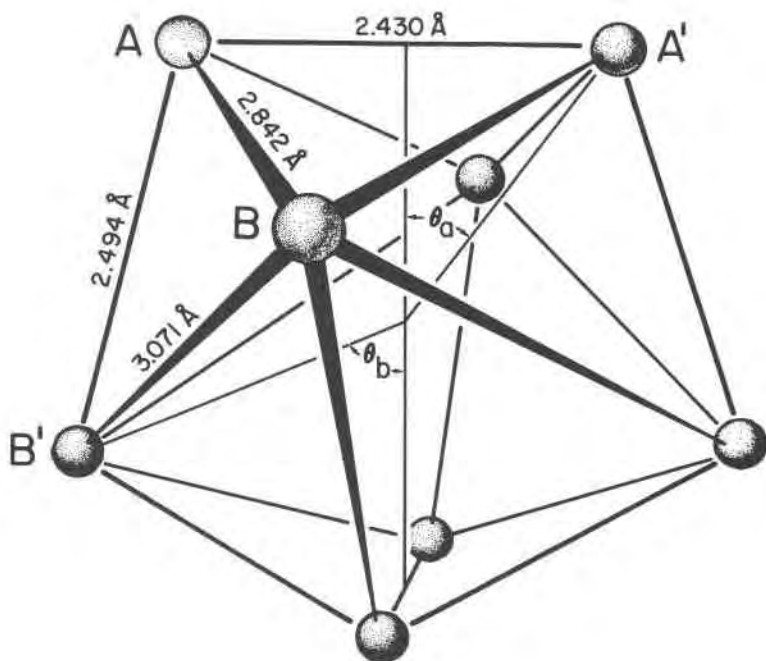


FIG. 5. The D_{2d} triangular dodecahedron (after Hoard and Silverton, 1963) for ZrO_8 in zircon.

elongated along the S_4 axis. In zircon the Si vibration spheroid is prolate along this axis in conformity with the distortions of the disphenoid (Table 3).

The two O-O edges shared with the ZrO_8 dodecahedron are short, 2.430 Å, opposite O-Si-O angles of 97.0° . The unshared edges are 0.32 Å longer, opposite O-Si-O angles of 116.1° (see Table 2). The Si-Zr repulsion across shared edges probably accounts for the elongation of the SiO_4 group along z .

The ZrO_8 polyhedron can best be described as a triangular dodecahedron (Hoard and Silverton, 1963). It has symmetry D_{2d} in contrast to the dodecahedron in garnet with $222 \equiv D_2$ symmetry. In zircon two edges are shared with SiO_4 groups and four with other dodecahedra (2.494 Å). There are two sets of unshared edges, eight at 2.842 Å and four at 3.071 Å (see Figure 5.) Similarly in garnet two edges are shared with SiO_4 tetrahedra and four with other dodecahedra, but there are only eight unshared edges; the remaining four are shared with YO_6 octahedra.

There are two non-equivalent Zr-O distances. The Zr-O bonds to the edges shared between tetrahedra and dodecahedra are both 2.268 Å;

those to edges shared by dodecahedra are 2.131 and 2.268 Å, as are those to the eight short unshared edges. The bonds to the four long unshared edges are 2.131 Å, as expected. There are also two non-equivalent X-O distances in the dodecahedra of garnet, but two *short* ones are opposite the edges shared by tetrahedra and dodecahedra and two *long* ones are opposite the longest unshared edges. The steric details of the dodecahedron in zircon are consistent with Pauling's rules, but in garnet such is not the case (Novak and Gibbs, 1971). An explanation for this discrepancy was offered by Gibbs and Smith (1965) who concluded that unreasonably long Y-O bond lengths and short unshared O-O distances would result if Pauling's rules were satisfied.

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