F(3)	0.2472 (2)	0	0.6498 (3)	1.74 (3)
F(4)	0.2670 (2)	0	0.1089 (3)	2.50 (4)
F(5)	0.0159 (1)	0.2061 (2)	0.3138 (2)	1.40 (2)

Table 2. *Selected geometric parameters* (Å)

Compound (1)			
Na—F(4)	2.184 (3)	Mn—F(5$^{\rm ii}$)	2.103 (2)
Na—F(4$^{\rm i}$)	2.184 (3)	Mn—F(5$^{\rm v}$)	2.103 (2)
Na—F(2)	2.242 (3)	Mn—F(5$^{\rm iv}$)	2.103 (2)
Na—F(2$^{\rm i}$)	2.242 (3)	Zr—F(4)	1.937 (3)
Na—F(5)	2.743 (2)	Zr—F(3$^{\rm vi}$)	2.005 (3)
Na—F(5$^{\rm ii}$)	2.743 (2)	Zr—F(5$^{\rm vii}$)	2.036 (2)
Na—F(5$^{\rm iii}$)	2.743 (2)	Zr—F(5$^{\rm viii}$)	2.036 (2)
Na—F(5$^{\rm i}$)	2.743 (2)	Zr—F(1$^{\rm vii}$)	2.082 (1)
Mn—F(3)	2.083 (2)	Zr—F(2$^{\rm vii}$)	2.135 (2)
Mn—F(3$^{\rm iv}$)	2.083 (2)	Zr—F(2$^{\rm ix}$)	2.135 (2)
Mn—F(5)	2.103 (2)		
Compound (2)			
Na—F(4)	2.179 (1)	Fe—F(5$^{\rm ii}$)	2.080 (1)
Na—F(4$^{\rm i}$)	2.179 (1)	Fe—F(5$^{\rm v}$)	2.080 (1)
Na—F(2)	2.223 (1)	Fe—F(5$^{\rm iv}$)	2.080 (1)
Na—F(2$^{\rm i}$)	2.223 (1)	Zr—F(4)	1.929 (1)
Na—F(5)	2.731 (1)	Zr—F(3$^{\rm vi}$)	2.003 (1)
Na—F(5$^{\rm ii}$)	2.731 (1)	Zr—F(5$^{\rm vii}$)	2.044 (1)
Na—F(5$^{\rm iii}$)	2.731 (1)	Zr—F(5$^{\rm viii}$)	2.044 (1)
Na—F(5$^{\rm i}$)	2.731 (1)	Zr—F(1$^{\rm vii}$)	2.074 (1)
Fe—F(3)	2.043 (1)	Zr—F(2$^{\rm vii}$)	2.138 (1)
Fe—F(3$^{\rm iv}$)	2.043 (1)	Zr—F(2$^{\rm ix}$)	2.138 (1)
Fe—F(5)	2.080 (1)		
Compound (3)			
Na—F(4)	2.174 (2)	Co—F(5$^{\rm ii}$)	2.053 (1)
Na—F(4$^{\rm i}$)	2.174 (2)	Co—F(5$^{\rm v}$)	2.053 (1)
Na—F(2)	2.206 (2)	Co—F(5$^{\rm iv}$)	2.053 (1)
Na—F(2$^{\rm i}$)	2.206 (2)	Zr—F(4)	1.930 (2)
Na—F(5)	2.731 (1)	Zr—F(3$^{\rm vi}$)	2.006 (1)
Na—F(5$^{\rm ii}$)	2.731 (1)	Zr—F(5$^{\rm vii}$)	2.043 (1)
Na—F(5$^{\rm iii}$)	2.731 (1)	Zr—F(5$^{\rm viii}$)	2.043 (1)
Na—F(5$^{\rm i}$)	2.731 (1)	Zr—F(1$^{\rm vii}$)	2.061 (1)
Co—F(3)	2.016 (1)	Zr—F(2$^{\rm vii}$)	2.135 (1)
Co—F(3$^{\rm iv}$)	2.016 (1)	Zr—F(2$^{\rm ix}$)	2.135 (1)
Co—F(5)	2.053 (1)		
Compound (4)			
Na—F(4)	2.168 (2)	Ni—F(5$^{\rm ii}$)	2.026 (1)
Na—F(4$^{\rm i}$)	2.168 (2)	Ni—F(5$^{\rm v}$)	2.026 (1)
Na—F(2)	2.190 (2)	Ni—F(5$^{\rm iv}$)	2.026 (1)
Na—F(2$^{\rm i}$)	2.190 (2)	Zr—F(4)	1.932 (2)
Na—F(5)	2.734 (1)	Zr—F(3$^{\rm vi}$)	2.008 (2)
Na—F(5$^{\rm ii}$)	2.734 (1)	Zr—F(5$^{\rm vii}$)	2.051 (1)
Na—F(5$^{\rm iii}$)	2.734 (1)	Zr—F(5$^{\rm viii}$)	2.051 (1)
Na—F(5$^{\rm i}$)	2.734 (1)	Zr—F(1$^{\rm vii}$)	2.052 (1)
Ni—F(3)	1.989 (2)	Zr—F(2$^{\rm vii}$)	2.138 (1)
Ni—F(3$^{\rm iv}$)	1.989 (2)	Zr—F(2$^{\rm ix}$)	2.138 (1)
Ni—F(5)	2.026 (1)		
Compound (5)			
Na—F(4)	2.174 (2)	Zn—F(5$^{\rm ii}$)	2.043 (1)
Na—F(4$^{\rm i}$)	2.174 (2)	Zn—F(5$^{\rm v}$)	2.043 (1)
Na—F(2)	2.205 (2)	Zn—F(5$^{\rm iv}$)	2.043 (1)
Na—F(2$^{\rm i}$)	2.205 (2)	Zr—F(4)	1.931 (2)
Na—F(5)	2.737 (1)	Zr—F(3$^{\rm vi}$)	2.007 (1)
Na—F(5$^{\rm ii}$)	2.737 (1)	Zr—F(5$^{\rm vii}$)	2.047 (1)
Na—F(5$^{\rm iii}$)	2.737 (1)	Zr—F(5$^{\rm viii}$)	2.047 (1)
Na—F(5$^{\rm i}$)	2.737 (1)	Zr—F(1$^{\rm vii}$)	2.059 (1)
Zn—F(3)	2.010 (1)	Zr—F(2$^{\rm vii}$)	2.134 (1)
Zn—F(3$^{\rm iv}$)	2.010 (1)	Zr—F(2$^{\rm ix}$)	2.134 (1)
Zn—F(5)	2.043 (1)		

Symmetry codes: (i) $-x, -y, -z$; (ii) $x, -y, z$; (iii) $-x, y, -z$; (iv) $-x, y, 1-z$; (v) $-x, -y, 1-z$; (vi) $1-x, y, 1-z$; (vii) $\frac{1}{2}+x, y-\frac{1}{2}, z$; (viii) $\frac{1}{2}+x, \frac{1}{2}-y, z$; (ix) $\frac{1}{2}-x, \frac{1}{2}-y, -z$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program used to solve and refine structure: *MolEN*. Molecular graphics: *ORTEP* (Johnson, 1965).

Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: AB1265). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Zirconium Tungstate

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Abstract

Zirconium tungstate, $Zr(WO_4)_2$, has been prepared by solid-state reaction at 1473 K. The structure was determined from X-ray and neutron powder diffraction data and refined by the Rietveld method. The final R indices are $R_F = 0.032$, $R_I = 0.027$ and $R_P = 0.065$. The structure contains WO_4 tetrahedra, each linked by three corners to three ZrO_6 octahedra; each tetrahedron has a terminal O atom with a short W—O distance. This arrangement is closely related to that of the $Zr(MoO_4)_2$ high-temperature form.

Comment

$M(XO_4)_2$ phases with M = Zr or Hf and X = Mo or W have been studied extensively by vibration spectroscopy (Auray & Tarte, 1982). In the case of the high-temperature form (HT) of $Zr(MoO_4)_2$, the results were correlated to the crystallographic features: the gap between the ν_3 bands originates from the distortion of the tetrahedral $(MoO_4)^{2-}$ anions (Auray, Quarton & Tarte, 1986). The presence of an O atom bonded only to Mo is related to an asymmetric distribution of π bonds around the Mo atom.

In order to establish such a correlation for the tungstate, the structure determination of $Zr(WO_4)_2$ was undertaken. It should be noted that $Zr(WO_4)_2$ and $Hf(WO_4)_2$ are probably isotypic: their powder diffraction spectra (JCPDS File Nos. 13–557 and 21–363, respectively) are very similar. The space group $P4_232$ was proposed by Trunov & Kovba (1967) for $Hf(WO_4)_2$.

The structure determination was performed from X-ray and neutron powder diffraction data. The refined cubic cell parameter, a = 9.1546 (2) Å, obtained from X-ray diffraction data, is in good agreement with previously reported values: a = 9.08 (Thoret, 1974), 9.159 (Chang, Scroger & Phillips, 1967) and 9.154 Å (Graham, Wadsley, Weymouth & Williams, 1959). A positive second harmonic generation test clearly confirms that $Zr(WO_4)_2$ is non-centrosymmetric. Consequently, the only space groups compatible with the observed diffraction lines are $P2_13$ and $P4_232$.

The integrated intensities of single X-ray diffraction lines were used to calculate the Patterson maps for these space groups. Only the $P2_13$ space group allows a correct interpretation of the Patterson maps. All the atomic sites were found and the refinement of their coordinates led to R_I = 0.048 for 46 independent *hkl*. At this stage of the refinement, the crystal structure of $Zr(WO_4)_2$ was correct. However, large e.s.d. values for the O-atom parameters, due to the major contribution of the W atoms to the structure factors, were found. Consequently, a neutron diffraction study was undertaken.

The neutron diffraction data were refined by the Rietveld method starting from the structure model previously obtained. The e.s.d. values of the atomic positional parameters were greatly improved and the isotropic displacement parameters were refined. The results are given in Table 1 and the observed, calculated and difference patterns appear in Fig. 1.

Zr atoms adopt sixfold coordination (Table 2); the O atoms are located at the corners of trigonal antiprisms resulting from the deformation of ZrO_6 octahedra. The mean Zr—O distance (2.07 Å) is equal to the sum of the ionic radii [$r_{O^{2-}}$ = 1.35 Å and $r_{Zr^{4+}}$ = 0.72 Å (Shannon, 1976)].

The W atoms are located in irregular tetrahedral O-atom environments. Both types of WO_4 tetrahedra are very similar with one short W—O distance (~1.72 Å)

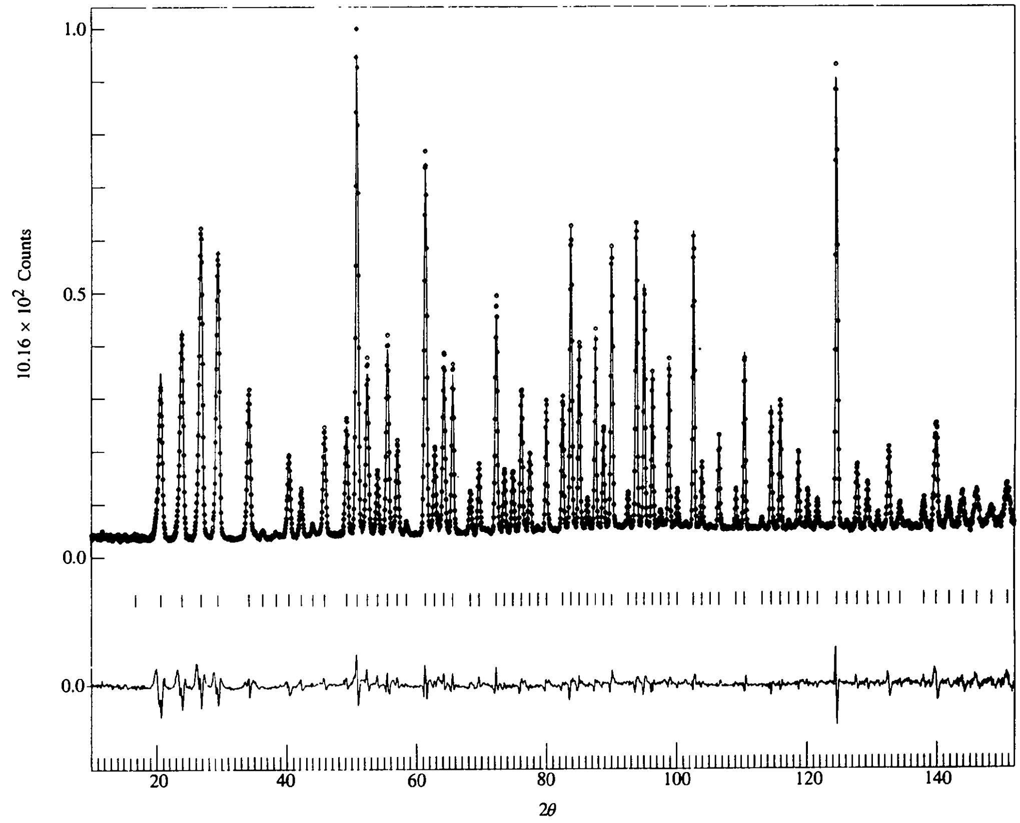

Fig. 1. Neutron powder diffraction diagrams of $Zr(WO_4)_2$: observed (circles) and calculated (solid). Vertical segments indicate the angular positions of possible Bragg reflections. The lower plot corresponds to the difference pattern (observed — calculated).

and three longer equal distances (~1.79 Å). These values are very close to the sum of the ionic radii (Shannon, 1976) and to the mean values frequently encountered for tungstates (Koster, Kools & Rieck, 1969; Kools, Koster & Rieck, 1970).

The ZrO_6 octahedra are isolated from one another, as well as from the WO_4 tetrahedra. Each polyhedron displays a threefold symmetry axis and the connection between the polyhedra occurs only at the corners [O(3) and O(4) atoms]. One ZrO_6 polyhedron is connected to six WO_4 tetrahedra, while one WO_4 tetrahedron is only connected to three ZrO_6 octahedra (Fig. 2). Consequently, each O(1) atom is only bonded to one W(1) atom, and each O(2) to one W(2), and the corresponding W(1)—O(1) and W(2)—O(2) distances are short.

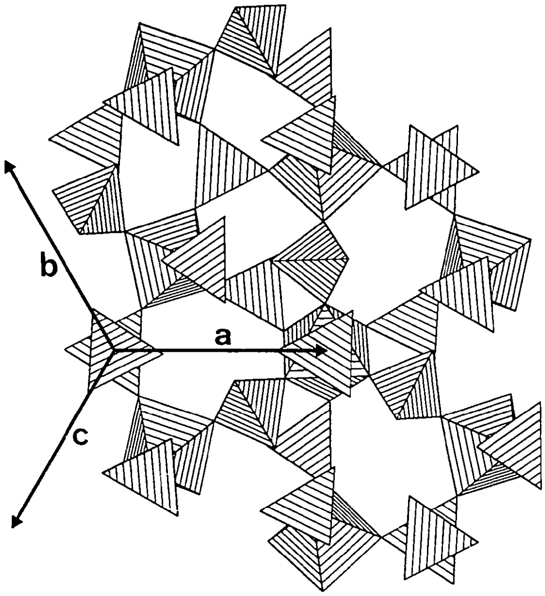

Fig. 2. Partial projection on (111) of the structure of $Zr(WO_4)_2$.

The structure of $Zr(WO_4)_2$ can be described as infinite chains of alternating ZrO_6 octahedra and WO_4 tetrahedra which propagate along the equivalent $[1\bar{1}0]$ directions. Three chains, along three directions at 120° from one another in each of the (111) planes, intersect at the ZrO_6 octahedra in order to build the three-dimensional network (Fig. 2). The environment of each ZrO_6 octahedron formed by six XO_4 tetrahedra can be compared to that encountered in HT-$Zr(MoO_4)_2$. In both phases, the ZrO_6 octahedra are located on threefold symmetry axes. In the two-dimensional structure of HT-$Zr(MoO_4)_2$, all the MoO_4 tetrahedra display short Mo—O vectors almost parallel to the threefold axis. They point alternately above and below the mean plane of the Zr and Mo atoms (Auray, Quarton & Tarte, 1986). In contrast, in $Zr(WO_4)_2$ half of the WO_4 tetrahedra that surround one ZrO_6 octahedron show a short W—O vector at ~70° from the threefold axis. This arrangement allows the orientation of short W—O vectors towards the centres of triangular faces of ZrO_6 octahedra. The corresponding O···O distances are short: O(1)···O(4) = 2.676 (6) Å.

The valence-bond analysis (Table 3), together with the identical valence electronic shell of the W and Mo atoms, suggests a similar distribution of π bonds in both $(XO_4)^{2-}$ anions (X = Mo, W): $(1\sigma + 0.5\pi)$ for the three long M—O distances and $(1\sigma + 1\pi)$ for the short M—O distance (Schroder, 1975).

Experimental

In agreement with the previous study of the binary diagram ZrO_2–WO_3 (Chang, Scroger & Phillips, 1967), $Zr(WO_4)_2$ can be obtained by solid-state synthesis. A stoichiometric mixture of ZrO_2 and WO_3 was finely ground and sealed in a silica tube under vacuum. It was then heated at 1423 K for 12 h. After grinding, the resulting white powder was heated further in air at 1473 K for 12 h in a platinum cup. Single crystals could not be obtained by fusion or flux growth. The density D_m was measured by pycnometry. Powder data were collected from 4 cm³ of the sample in a vanadium container.

Crystal data

$Zr(WO_4)_2$
M_r = 586.92
Cubic
$P2_13$
a = 9.1546 (2) Å
V = 767.22 (5) Å³
Z = 4
D_x = 5.081 Mg m^{-3}
D_m = 4.90 (5) Mg m^{-3}
Cu $K\alpha$ radiation
λ = 1.54178 Å

Cell parameters from 46 reflections of X-ray powder diffraction pattern
θ = 5–41.5°
Philips PW1050-25 diffractometer
Si as internal standard (Draggo, 1986)
T = 293 K
White

Data collection

D1A diffractometer
177 measured reflections

Neutrons
λ = 1.9090 Å
θ = 8–76°

Refinement

R_F = 0.032
R_I = 0.027
R_P = 0.065
Rietveld (1969) method adapted by Hewat (1986)
Asymmetry correction for $\theta < 35°$

Isotropic thermal agitation
32 parameters
Nuclear scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.6)

Table 1. *Fractional atomic coordinates and isotropic displacement parameters* (Å²)

	x	y	z	B_{iso}
Zr	0.7515 (3)	x	x	1.09 (4)
W(1)	0.3509 (3)	x	x	1.26 (9)
W(2)	0.0913 (3)	x	x	1.52 (9)
O(1)	0.2414 (4)	x	x	2.15 (5)
O(2)	0.9833 (3)	x	x	3.45 (5)
O(3)	0.3058 (3)	0.3200 (4)	0.5381 (3)	1.3 (1)
O(4)	0.1974 (3)	0.1883 (4)	0.9573 (3)	3.3 (1)

Table 2. *Selected geometric parameters* (Å, °)

ZrO$_6$ polyhedron		
Zr—O(3^{i,ii,iii})	2.092 (4)	(× 3)
O(3^{i,ii})—O(3^{ii,iii})	3.003 (6)	(× 3)
O(3^{i,ii,iii})—O(4^{iii,i,ii})	2.868 (7)	(× 3)
Zr—O(4^{i,ii,iii})	2.051 (4)	(× 3)
O(4^{i,ii})—O(4^{ii,iii})	2.921 (6)	(× 3)
O(3^{i,ii,iii})—O(4^{ii,iii,i})	2.928 (7)	(× 3)
O(3^{i,ii})—Zr—O(3^{ii,iii})	91.72 (2)	(× 3)
O(3^{i,ii,iii})—Zr—O(4^{iii,i,ii})	87.57 (2)	(× 3)
O(4^{i,ii})—Zr—O(4^{ii,iii})	90.80 (2)	(× 3)
O(3^{i,ii,iii})—Zr—O(4^{ii,iii,i})	89.92 (2)	(× 3)

WO$_4$ polyhedra

W(1)	O(1)	O(3)	O(3^{iv})	O(3^{v})
O(1)	1.736 (4)	2.871 (6)	2.871 (6)	2.871 (7)
O(3)	109.22 (1)	1.785 (3)	2.920 (6)	2.920 (6)
O(3^{iv})	109.22 (1)	109.72 (1)	1.785 (3)	2.920 (6)
O(3^{v})	109.22 (2)	109.72 (1)	109.72 (2)	1.785 (4)

W(2)	O(2^{vi})	O(4^{vii})	O(4^{viii})	O(4^{ix})
O(2^{vi})	1.713 (3)	2.724 (5)	2.724 (6)	2.724 (5)
O(4^{vii})	101.71 (2)	1.799 (3)	3.051 (6)	3.051 (6)
O(4^{viii})	101.71 (2)	115.99 (3)	1.799 (4)	3.051 (6)
O(4^{ix})	101.71 (2)	115.99 (3)	115.99 (3)	1.799 (4)

Symmetry codes: (i) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$; (ii) $\frac{1}{2} + y, \frac{3}{2} - z, 1 - x$; (iii) $\frac{3}{2} - z, 1 - x, \frac{1}{2} + y$; (iv) z, x, y; (v) y, z, x; (vi) $x - 1, y - 1, z - 1$; (vii) $x, y, z - 1$; (viii) $z - 1, x, y$; (ix) $y, z - 1, x$.

Table 3. *Lengths and valences of M—O bonds for* Zr(XO$_4$)$_2$ *compounds*

	β-Zr(MoO$_4$)$_2$^{a}		Σs	Zr(WO$_4$)$_2$^{b}		Σs
X—O (Å)	1.69	1.76 (× 3)		1.72	1.79 (× 3)	
s^c	1.80	1.47 (× 3)	6.21	1.70	1.42 (× 3)	5.96
Zr—O (Å)	2.08 (× 3)	2.09 (× 3)		2.05 (× 3)	2.09 (× 3)	
s^c	0.68 (× 3)	0.66 (× 3)	4.02	0.73 (× 3)	0.66 (× 3)	4.17

References: (*a*) Auray, Quarton & Tarte (1986); (*b*) this work; (*c*) Brese & O'Keeffe (1991).

A list of 177 neutron diffraction reflections has been deposited with the IUCr (Reference: DU1110). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Low-Pressure Polymorph of Co$_3$Al$_2$Si$_3$O$_{12}$

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Abstract

The structure of cobalt aluminium silicate garnet, Co$_3$Al$_2$Si$_3$O$_{12}$, has been redetermined from diffractometer data. Comparison of the present refinement with the published refinements for the M_3^{2+}Al$_2$Si$_3$O$_{12}$ garnets suggests that two isostructural phases exist for the Co$_3$Al$_2$Si$_3$O$_{12}$ garnet which are dependent on the pressure.

Comment

The title compound [hereafter Co(β) garnet] is isostructural with Co$_3$Al$_2$Si$_3$O$_{12}$ [hereafter Co(α) garnet: a = 11.455 (2) Å, x = 0.03421 (16), y = 0.05138 (15), z = 0.65367 (16) (Ohashi, Fujita & Osawa, 1981)]. Their mean Co—O distances are similar, but the ratios of the octahedral–dodecahedral shared edge (O$\cdots$O^{v}) distance to the dodecahedral–dodecahedral shared edge (O$^{v}\cdots$O^{ix}) distance are different. Table 3 summarizes the ratios (O$\cdots$O^{v})/(O$^{v}\cdots$O^{ix}) and the tetrahedral position angles (Born & Zemann, 1964) in the M_3^{2+}Al$_2$Si$_3$O$_{12}$ garnets. As shown in Fig. 2, the tetrahedral position angle is linearly dependent on the ratio (O$\cdots$O^{v})/(O$^{v}\cdots$O^{ix}).

From the Si—O distances [1.627 (2) Å in Co(α) garnet and 1.634 (1) Å in Co(β) garnet] the electronegativities of the dodecahedral (double tetrahedral) Co(α) and Co(β) atoms are estimated to be 1.8 and 1.6, respectively, on Pauling's scale (Ohashi, Fujita & Osawa, 1981).

Structures for Co-åkermanite, Ca$_2$CoSi$_2$O$_7$, in which the Co atom is tetrahedrally coordinated by O atoms, were reported by Kimata (1983) and Hagiya, Ohmasa & Iishi (1993). Kimata (1983) obtained smaller unit-cell dimensions [a = 7.8258 (4), c = 5.0148 (5) Å, V = 307.13 (4) Å^3] than those obtained by Hagiya *et al.* (1993) [a = 7.8417 (6), c = 5.0249 (3) Å, V = 308.99 Å^3]. The mean Si—O distances in the two Co-åkermanites were found to be 1.608 (Kimata, 1983) and 1.618 (3) Å (Hagiya *et al.*, 1993). These Si—O distances suggest that the electronegativities of the tetrahedral Co atoms are 1.8 and 1.6, respectively, on Pauling's scale (Ohashi, 1984).

The variation of the electronegativities of the tetrahedral Co atoms in garnet and åkermanite suggest that

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