

## Crystal Structure of Magnesium Divanadate, $\text{Mg}_2\text{V}_2\text{O}_7$

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**Abstract.**  $\text{Mg}_2\text{V}_2\text{O}_7$  crystals were grown slowly from a melt of  $\text{MgCO}_3$  and  $\text{V}_2\text{O}_5$ ; triclinic,  $P\bar{1}$ ,  $a=13.767$  (7),  $b=5.414$  (3),  $c=4.912$  (2) Å,  $\alpha=81.42$  (4),  $\beta=106.82$  (4) and  $\gamma=130.33$  (4)°,  $Z=2$ ,  $\rho_m=3.1$ ,  $\rho_x=3.24$  g cm<sup>-3</sup>. The structure, refined by full-matrix least-squares methods with 1770 symmetry-independent reflexions, has chains of  $\text{V}_2\text{O}_7$  groups with long VO bridges between these groups. These V–O(–V) bond lengths are 1.817 and 1.784 Å with a V–O–V angle of 140.6°, while the average terminal V–O bond length is 1.694 Å.

**Introduction.** Intensities were obtained from a single crystal with dimensions 0.1 × 0.1 × 0.3 mm ( $\mu R=0.5$ ) on a Syntex  $P\bar{1}$  automatic diffractometer with scintillation counter and pulse-height discrimination (Mo  $K\alpha$ , graphite monochromatized,  $\theta-2\theta$  with variable scan rate,  $2\theta \leq 80^\circ$ ). A standard reflexion was measured at intervals of 50 reflexions and backgrounds were determined at 1° from either side of the peaks. 1900 symmetry-independent reflexions were obtained and corrected for background and Lorentz–polarization but not for absorption. Those with intensity less than  $3\sigma$ , with  $\sigma$  determined from the counting statistics, were considered unobserved. The space group was chosen on the basis of the distribution of  $\langle E^2 - 1 \rangle$  and a trial structure obtained from the Patterson function.

The structure was refined by full-matrix least-squares methods using the program written by J. S. Stephens for the CDC 6400. The atomic scattering curves for  $\text{Mg}^{2+}$ ,  $\text{V}^{3+}$  and  $\text{O}^-$  were obtained from *International Tables for X-ray Crystallography* (1963) and corrected for dispersion. Weights,  $\omega=(0.15 + 0.0012F_o + 0.0005F_o^2)^{-1}$ , were chosen so that  $\Delta F$  would

be independent of  $F_o$ . Anisotropic thermal parameters and extinction parameters, calculated by the method of Larson (1968), were introduced after convergence with isotropic thermal parameters. The refinement was terminated when all the shifts were less than  $\sigma/3$  and  $R=0.022$  and  $R_w = \{\sum \omega(F_o - F_c)^2 / \sum \omega F_o^2\}^{1/2} = 0.027$ . The final atomic parameters are listed in Table 1 and the bond lengths and angles are in Table 2.\*

**Discussion.** The  $\text{MgO-V}_2\text{O}_5$  system has been the object of numerous studies (Lucas, Weddle & Preece, 1955; King & Suber, 1955; Zyazev & Esin, 1958; Weller & King, 1962; Kohlmuller & Perraud, 1964; Pollard, 1964; Matvieicheva, Ezhkova, Zaitsev & Lyubarskii, 1969; Wollast & Tazairt, 1968; Speranskaya, 1971). Although all agree that  $\text{Mg}_3\text{V}_2\text{O}_8$  and  $\text{Mg}_2\text{V}_2\text{O}_7$  are stable, there has been controversy concerning the stability of  $\text{MgV}_2\text{O}_6$  and  $\text{Mg}_3\text{V}_4\text{O}_{13}$  (Speranskaya, 1971).  $\text{Mg}_2\text{V}_2\text{O}_7$  is reported to have one (Pollard, 1964) or two solid-state transformations (Wollast & Tazairt, 1968).

The structure of  $\text{Mg}_2\text{V}_2\text{O}_7$  consists of chains of  $\text{V}_2\text{O}_7$  groups formed from what, to a first approximation, can be described as  $\text{VO}_4$  tetrahedra. These  $\text{V}_2\text{O}_7$  groups are linked by edge-sharing across centres of symmetry and involve a weak fifth V–O bond [ $\text{V}(1)-\text{O}(7')=2.869$  Å] at one end and a somewhat

\* The observed and calculated structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30531 (12 pp., 1 microfiche). Copies may be obtained from The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Positional parameters and thermal parameters* ( $\times 10^4$ ) *for*  $\text{Mg}_2\text{V}_2\text{O}_7$  *with standard errors in parentheses*

$U_{ij} = (2\pi b_i b_j)^{-1} \beta_{ij}$ . The  $\beta_{ij}$  appear in the structure factor expression as  $\exp [-(\beta_{11}h^2 + \dots + 2\beta_{12}hk + \dots)]$  and the  $b_i$ 's are reciprocal-lattice parameters.

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Mg(1)	0.08370 (8)	0.3767 (2)	0.5095 (2)	88 (3)	68 (4)	63 (3)	52 (3)	6 (3)	1 (3)
Mg(2)	0.41687 (8)	0.6187 (2)	0.4229 (2)	80 (3)	73 (4)	72 (3)	50 (3)	6 (3)	8 (3)
V(1)	0.63934 (4)	−0.0702 (1)	0.03708 (8)	72 (2)	67 (2)	41 (2)	43 (1)	3 (1)	7 (1)
V(2)	0.86140 (4)	−0.0632 (11)	−0.14070 (8)	68 (2)	62 (2)	41 (2)	36 (1)	−3 (1)	1 (1)
O(1)	0.7075 (2)	−0.2036 (5)	−0.1055 (4)	110 (7)	156 (10)	120 (7)	85 (7)	28 (6)	−18 (7)
O(2)	0.9523 (2)	−0.0124 (5)	0.2089 (3)	120 (7)	82 (8)	43 (6)	60 (6)	−11 (5)	−1 (5)
O(3)	0.7651 (2)	0.2893 (5)	0.1865 (4)	135 (8)	117 (9)	115 (7)	50 (7)	−26 (6)	−29 (7)
O(4)	0.9334 (2)	0.2896 (5)	−0.3044 (4)	131 (7)	105 (8)	108 (7)	88 (7)	33 (6)	33 (6)
O(5)	0.4588 (2)	0.0313 (5)	0.2352 (4)	117 (7)	91 (8)	61 (6)	75 (6)	−6 (5)	4 (6)
O(6)	0.2123 (2)	0.3753 (5)	0.3636 (4)	69 (6)	95 (8)	107 (7)	42 (6)	30 (5)	−14 (6)
O(7)	0.4386 (2)	0.3242 (5)	0.7109 (4)	125 (7)	119 (9)	80 (6)	91 (7)	40 (5)	38 (6)

Table 2. Bond lengths (Å) and angles (°) in  $Mg_2V_2O_7$  with standard errors in parentheses

Mg(1)—O(2)i 2.083 (3)	Mg(2)—O(1)ii 2.221 (3)
—O(6)ii 2.062 (4)	—O(6)ii 2.157 (3)
—O(2)ii 2.089 (3)	—O(7)ii 2.081 (4)
—O(4)i 2.246 (4)	—O(5)ii 2.049 (4)
—O(4)ii 2.050 (4)	—O(7)i 2.095 (4)
—O(3)ii 1.992 (3)	—O(5)i 2.104 (3)
O(2)i—Mg(1)—O(6)ii 79.0 (1)	O(1)ii—Mg(2)—O(6)ii 70.6 (2)
—O(2)ii 82.9 (1)	—O(7)ii 86.7 (2)
—O(4)i 97.1 (1)	—O(5)ii 111.5 (1)
—O(4)ii 100.9 (1)	—O(7)i 79.1 (1)
—O(3)ii 165.7 (2)	—O(5)i 171.1 (2)
O(6)ii—Mg(1)—O(2)ii 93.8 (2)	O(6)ii—Mg(2)—O(7)ii 101.9 (1)
—O(4)i 170.8 (1)	—O(5)ii 93.3 (2)
—O(4)ii 109.3 (2)	—O(7)i 149.1 (1)
—O(3)ii 89.3 (2)	—O(5)i 112.4 (2)
O(2)ii—Mg(1)—O(4)i 77.4 (2)	O(7)ii—Mg(2)—O(5)ii 159.5 (1)
—O(4)ii 156.9 (2)	—O(7)i 81.7 (2)
—O(3)ii 89.8 (1)	—O(5)i 84.5 (1)
O(4)i—Mg(1)—O(4)ii 79.5 (2)	O(5)ii—Mg(2)—O(7)i 92.2 (2)
—O(3)ii 93.3 (2)	—O(5)i 77.1 (1)
O(4)ii—Mg(1)—O(3)ii 90.7 (2)	O(7)i—Mg(2)—O(5)i 98.4 (1)
V(1)—O(1) 1.817 (4)	V(1)—O(1) 1.784 (4)
—O(3) 1.629 (3)	—O(2) 1.744 (3)
—O(5) 1.702 (3)	—O(4) 1.682 (3)
—O(7) 1.710 (3)	—O(6) 1.707 (3)
—O(7)ii 2.869 (3)	—O(2)ii 2.440 (4)
O(1)—V(1)—O(3) 105.7 (2)	O(1)—V(2)—O(2) 104.3 (2)
—O(5) 109.5 (2)	—O(4) 109.2 (2)
—O(7) 110.6 (2)	—O(6) 92.9 (2)
O(3)—V(1)—O(5) 107.9 (2)	O(2)—V(2)—O(4) 111.7 (1)
—O(7) 109.2 (2)	—O(6) 123.2 (2)
O(5)—V(1)—O(7) 113.7 (2)	O(4)—V(2)—O(6) 112.8 (2)
O(7)ii—V(1)—O(1) 67.6 (1)	O(2)ii—V(2)—O(1) 168.3 (2)
—O(3) 171.5 (2)	—O(2) 77.8 (2)
—O(5) 70.8 (1)	—O(4) 111.7 (2)
—O(7) 78.6 (1)	—O(6) 123.2 (2)
V(1)—O(1)—V(2) 140.6 (2)	

Symmetry transformations are exclusive of translations with  $i = x, y, z$  and  $ii = -x, -y, -z$ .

stronger fifth V—O bond [V(2)—O(2)' = 2.440 Å] at the other end, as shown in Fig. 1. Adjacent chains form sheets lying in the (001) plane, as in thortveitite (Cruikshank, Lynton & Barclay, 1962), with the  $b$  axis in  $Mg_2V_2O_7$  comparable with the  $\frac{1}{2}(-a+b)$  axis in thortveitite. Adjacent sheets are separated by Mg cations which share oxygen atoms with these sheets as seen in Fig. 2. Each of the terminal oxygen atoms of the  $V_2O_7$  groups, except for O(3), are shared with two Mg ions. Each of the Mg ions is bonded to six oxygen atoms. All of these are terminal oxygen atoms in the case of Mg(1) while one of the oxygen atoms bonded to Mg(2) is a bridging oxygen atom.

Each  $MgO_6$  group shares two edges with neighbouring  $MgO_6$  groups to form chains which consist of either all  $Mg(1)O_6$  or  $Mg(2)O_6$  groups. Each  $Mg(1)O_6$  group shares only one oxygen atom with a  $Mg(2)O_6$ . If O(3) were bonded to Mg(2) rather than O(1) the sheet of cation octahedra would be similar to those in thortveitite (Fig. 3). The oxygen atoms in thortveitite are hexagonally close-packed with the cations lying in octahedral sites in alternate layers interleaved with the Si—O—Si portion of the disilicate ion. The octa-

hedral sites are filled so that each  $MO_6$  group shares three edges and each of these oxygen atoms is shared by two M ions. The filled octahedral sites are in sixfold rings about an empty site and the Si—O—Si group sits in an octahedral site opposite to this empty site.

The two  $VO_4$  groups in the anion are quite distinct (Table 2). The V(1)—O(3) is the shortest of the terminal V—O bond lengths since this oxygen atom is bonded to only one divalent cation. The V(2)— $O_4$  tetrahedron is distorted with the fifth V(2)—O interaction, involving O(2)', resulting in O—V—O bond angles in the tetrahedron ranging from 92.9 to 123.2° (Fig. 1).

The  $MgO_6$  octahedra are irregular with Mg—O bond lengths ranging from 1.992 to 2.246 Å about Mg(1) and 2.049 to 2.221 Å about Mg(2). The shortest of these bonds involves O(3), the same oxygen atom that has the shortest V—O bond length.

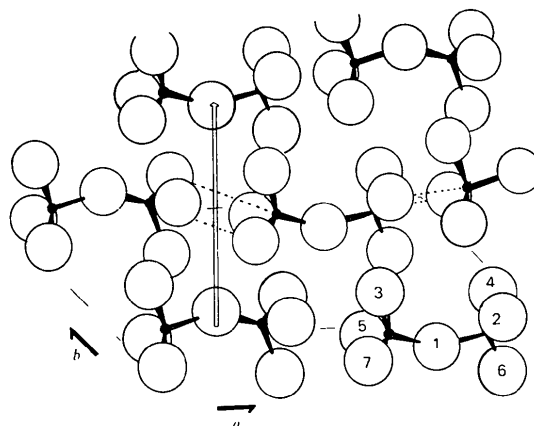


Fig. 1. The anions in the structure of  $Mg_2V_2O_7$  are shown projected down the  $c$  axis. The large circles represent oxygen atoms and the filled circles the vanadium atoms. The dotted lines represent the weak interactions between the vanadium ion in one anion and an oxygen atom in another. The open arrow represents the  $b$  axis translation of the thortveitite structure.

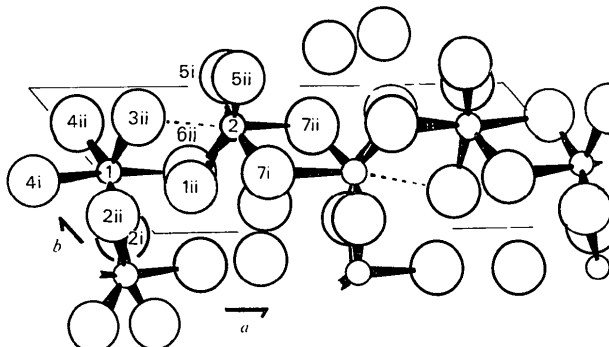


Fig. 2. The cationic polyhedra in  $Mg_2V_2O_7$  are shown in a layer parallel to that of Fig. 1. The large open circles represent oxygen atoms and the small ones represent Mg ions. The dotted lines indicate the bond which is broken in going from the thortveitite structure to that of  $Mg_2V_2O_7$ .

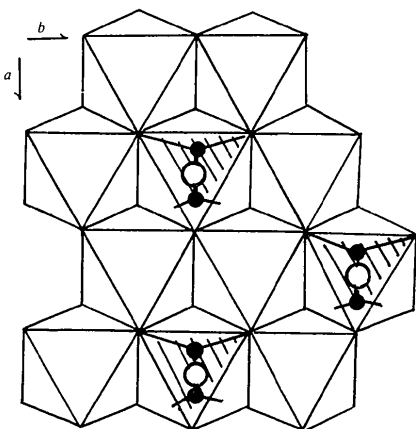


Fig. 3. An idealization of the cationic sheet structure in thortveitite. The cations are at the centre of all the octahedra that do not have ruled surfaces. The oxygen atoms lie at the corners of the polyhedra and the disilicate ion, on the ruled surface is indicated.

The structure of  $\text{Mg}_2\text{V}_2\text{O}_7$  differs from any previously reported  $\text{M}_2\text{X}_2\text{O}_7$  structures. Although X is tetrahedrally coordinated, the perturbations, particularly at V(2), due to the fifth neighbour, are large. In  $\alpha\text{-Zn}_2\text{V}_2\text{O}_7$  (Gopal & Calvo, 1973) the V–O–V angle is  $149.5(8)^\circ$ , the O–V–O(–V) bond angles are slightly less than ideal with those involving only terminal oxygen atoms slightly greater than ideal. Further, the V–O(–V) bond, since Zn ions are not bonded to the bridging oxygen atom, is  $1.775(4) \text{ \AA}$  and the average V–O bond involving terminal oxygen atoms is  $1.697 \text{ \AA}$ .

The short interaction between anion groups related by the *a* axis translation has already been noted in thortveitite (Cruickshank, Lynton & Barclay, 1962). The ability of  $\text{V}^{5+}$  to change easily from fourfold to five or sixfold coordination allows the present structure to be stable in divanadate rather than in diphosphate or disilicate systems.

The relationship between the thortveitite structure and that of  $\text{Mg}_2\text{V}_2\text{O}_7$  has been emphasized in the choice of the unit cell in the latter structure. The *c* axis length is twice as long in  $\text{Mg}_2\text{V}_2\text{O}_7$  because of non-linear V–O–V groups on adjacent anions are related by a centre of symmetry. The *b* axis length in  $\text{Mg}_2\text{V}_2\text{O}_7$  corresponds to anions related by the centring  $(-a/2 + b/2)$  in thortveitite, whereas the *a* axes are of comparable dimensions in the two systems.

All the members of the thortveitite series that undergo a phase transformation do so at the expense of a non-linear X–O–X grouping and reduced coordination at some fraction of the cations (Robertson & Calvo,

1970). In  $\alpha\text{-Mg}_2\text{P}_2\text{O}_7$ , the low-temperature polymorph of  $\text{Mg}_2\text{P}_2\text{O}_7$ , the sixth nearest oxygen atom to Mg(2) is the bridging oxygen atom ( $3.060 \text{ \AA}$ )\* rather than the terminal oxygen atom [ $\text{Mg}(2)\text{-O}(31T) = 3.373 \text{ \AA}$ ] to which it is bonded in thortveitite-like  $\beta\text{-Mg}_2\text{P}_2\text{O}_7$ . The displacements of adjacent bridging oxygen atoms from collinearity with the P–P vector in a sheet are related alternately by a screw axis and a centre of symmetry.

The strong bond between the bridging oxygen atom and one of the cations in  $\text{Mg}_2\text{V}_2\text{O}_7$  allows both for sixfold cationic coordination and a bent V–O–V moiety. Here the displacements of adjacent bridging oxygen atoms are related by centres of symmetry. There appears to be a close relationship between the structures of  $\text{Mg}_2\text{V}_2\text{O}_7$  and  $\alpha$  and  $\beta\text{-Mg}_2\text{P}_2\text{O}_7$ . Thus a possible first-order phase transformation in  $\text{Mg}_2\text{V}_2\text{O}_7$  resulting in a thortveitite-like structure would be expected.

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\* These results are based upon a new refinement of the  $\alpha \text{ Mg}_2\text{P}_2\text{O}_7$  structure (Calvo, 1967) using data collected with a Syntex PT diffractometer.

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