as well as Ru at both positions can be understood, since the ions have almost the same radii, 0·605 and 0·620 Å respectively (Shannon, 1976), and both $BaTiO_3$ and $BaRuO_3$ occur with the 6*L* structure.

The distance between the metal atoms in the $[Ru(1),Ti(2)]_2O_9$ group is too short to form regular face-shared octahedra. Because of the repulsion between the metal atoms, they are not exactly at the centers of the face-sharing octahedra. This results in a shorter O(1)—O(1) distance in the common face and in the angle O(1)—metal—O(2) being larger than 90°.

The metal—metal distance is very short (2·515 Å), suggesting intermetallic bonding. This intermetallic bond is also reported in the 9*L*-$BaRuO_3$ structure, in which the Ru—Ru distance is 2·55 Å (Donohue, Katz & Ward, 1965).

In $Ba_3SrNb_2O_9$ (Zandbergen & IJdo, 1983) the Nb—Nb distance is 2·97 Å, while in $Ba_3SrRu_2O_9$ (Zandbergen & IJdo, 1984) the Ru—Ru distance is 2·67 Å. This difference is due to the atomic radius of Nb^{5+}, which is larger than that of Ru^{5+}, 0·64 Å and 0·565 Å respectively (Shannon, 1976). The difference in Ru—Ru distance in $Ba_3TiRu_2O_9$ and $Ba_3SrRu_2O_9$ is probably the result of the difference in valence of the Ru atoms, which is respectively 4+ and 5+.

In an undeformed packing with ideal octahedra the axial ratio $c/a = \sqrt{6} = 2{\cdot}449$ (Zandbergen & IJdo, 1983). For $Ba_3TiRu_2O_9$ the axial ratios are 2·455 at 300 K and 2·456 at 1·2 K. A tilt around the threefold axes decreases the lattice parameter *a* and thus increases *c*/*a*. Because the *c*/*a* values are close to the expected value, we expect that the tilt is zero.

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Structure of the Intermediate Phase, $Li_{2.09}W_{0.91}Nb_{0.09}O_4$, in the Li_2WO_4–Li_3NbO_4 System

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Abstract. $M_r = 254{\cdot}2$, triclinic, $P\bar{1}$, $a = 7{\cdot}967$ (2), $b = 7{\cdot}774$ (1), $c = 5{\cdot}271$ (1) Å, $\alpha = 90{\cdot}61$ (2), $\beta = 103{\cdot}41$ (2), $\gamma = 105{\cdot}81$ (2)°, $V = 304{\cdot}6$ (1) Å^3, $Z = 4$, $D_m = 5{\cdot}518$, $D_x = 5{\cdot}543$ (2) g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 367$ cm^{-1}, $F(000) = 437$, $T = 293$ K, final $R = 0{\cdot}047$ for 2125 observed reflections. The O atoms are in approximate cubic close-packing with (W,Nb) atoms in octahedral interstices, arranged so that $(W,Nb)_4O_{16}$ groups are created. These groups are connected through a three-dimensional framework of edge-sharing LiO_6 octahedra and Li_4O_{10} groups of edge-sharing LiO_4 tetrahedra.

Introduction. The niobium–tungsten oxides containing alkali metals are of considerable interest as solid-state ionic conductors. Li^+ ions especially have been shown to be mobile in a voltage gradient, and therefore the Li–W–Nb–O system has been investigated at this laboratory (Hörlin, Marinder & Nygren, 1982).

The subsystem Li_2WO_4–Li_3NbO_4 was searched for non-stoichiometric compounds with partially occupied lithium sites. The phase analysis revealed one intermediate compound, which could be prepared as a single phase, with the composition $Li_{2.09}W_{0.91}Nb_{0.09}O_4$. This article will describe the results of the single-crystal

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X-ray structure determination. The conductivity measurements will be published elsewhere.

Experimental. Starting materials: Li_2WO_4 and Li_3NbO_4, prepared by heating appropriate amounts of Li_2CO_3 (Mallinckrodt, analytical reagent), WO_3 (99·9% pure, Koch-Light Lab.) and Nb_2O_5 (Merck, optipure, purified of oxide fluorides at 1275 K in air) in Pt crucibles at 875 K, one week. Purity checked by analysis of X-ray powder patterns. Single-phase sample, composition $Li_{2.09}W_{0.91}Nb_{0.09}O_4$, confirmed by density measurements, obtained by mixing Li_2WO_4 and Li_3NbO_4 in the mole-ratio 10:1 and kept in sealed Pt ampoules at 1175 K, two days. Unit-cell dimensions from Guinier X-ray powder pattern,* refined with program *PIRUM* (Werner, 1969), internal standard KCl ($a = 6{\cdot}2930$ Å at 298 K, Hambling, 1953). Density determined from apparent loss of weight in *n*-hexane, density of the liquid calibrated with Ge crystal ($D = 5{\cdot}326$ g cm^{-3}) at 298 K (Straumanis & Aka, 1952).

Diffraction data from a small, irregular, colourless single crystal mounted on a Philips PW 1100 computer-controlled automatic four-circle diffractometer with a graphite monochromator. Data corrected for Lorentz and polarization as well as absorption effects; anomalous-scattering-factor values for uncharged atoms from *International Tables for X-ray Crystallography* (1974); calculations performed with *SHELX*76 (Sheldrick, 1976) on the Amdahl 470/7A and VAX computing systems. Details of data collection and refinement are given in Table 1.

Solution of structure with Patterson and difference Fourier methods, refinement by full-matrix least-squares techniques (based on *F*) in space group $P\bar{1}$. Heavy metals treated as W. Occupational parameters determined for W and Li by alternate refinements of isotropic thermal parameters and occupancy factors. 0·95 (1) for W agreed well with the 0·96 derived from density measurements. 7·1 out of 8·36 Li atoms found, the rest is probably randomly distributed over some of the available octahedral and tetrahedral interstices. $(\Delta/\sigma)_{\max} = 0{\cdot}005$, $(\Delta\rho)_{\max} = 4{\cdot}6$ e Å^{-3} (in the vicinity of W) and $(\Delta\rho)_{\min} = -4{\cdot}9$ e Å^{-3} in final difference Fourier map. *E* statistics as a function of $\sin\theta/\lambda$ gave the value 0·82, intermediate between the theoretical values 0·97 for centrosymmetry and 0·74 for non-centrosymmetry (Karle, Dragonette & Brenner, 1965). Attempts to refine the structure in the non-centrosymmetric space group ($P1$) resulted in an increase in e.s.d.'s by 50% and a decrease of the *R* value from 0·047 to 0·044. The structure is thus probably best described in $P\bar{1}$.

Table 1. *Details of the data collection and refinement*

Crystal size (mm)	0·076 × 0·038 × 0·052
Absorption-correction transmission factors	0·16–0·60
Scan type	ω–2θ
Scan speed (°s^{-1})	0·015
Scan width (°)	1·6
$(\sin\theta/\lambda)_{\max}$(Å^{-1})	0·8072
Range of *hkl*	$-12 \le h \le 12, -12 \le k \le 12, 0 \le l \le 8$
Standard reflections	$1\bar{3}1, 12\bar{4}, \bar{3}42$
No. of reflections measured	2924
No. of unique reflections	2718
$R_{\rm int}$	0·018
No. of unobserved reflections	593 $[I < 2{\cdot}5\sigma(I)]$
No. of parameters refined	71
Final *R*	0·047
R_w (unit weights)	0·047

Discussion. The final positional, thermal and occupancy parameters are given in Table 2. Relevant interatomic distances are presented in Table 3.*

The structure of $Li_{2.09}W_{0.91}Nb_{0.09}O_4$, thus derived, can be described as a distorted cubic close-packed arrangement of O atoms. The (W,Nb) atoms occupy $\frac{1}{4}$ of the octahedral interstices, and the Li atoms are distributed over $\frac{1}{4}$ of the octahedrally and $\frac{1}{8}$ of the tetrahedrally coordinated sites. The structure is composed of identical sheets of metal—oxygen polyhedra, as is shown in Fig. 1. The sheets are stacked on top of each other and shifted so that identically numbered O atoms coincide. The (W,Nb) atoms are arranged in $(W,Nb)_4O_{16}$ tetramers of edge-sharing $(W,Nb)O_6$ octahedra, connected through Li_4O_{10} tetramers of edge-sharing LiO_4 tetrahedra and rows of four edge-sharing LiO_6 octahedra. The lithium–oxygen polyhedra form a three-dimensional framework, since the LiO_6 octahedra rows are also joined to each other by edge-sharing in a staircase-like way perpendicular to the projection plane of the structure (*cf.* Fig. 2*a*).

The metal–metal repulsion within the $(W,Nb)_4O_{16}$ group is obvious (Fig. 2*b*). The metal atoms are shifted from the centres of the octahedra so that shorter bonds (1·78–1·80 Å) are formed to the O atoms not shared with other $(W,Nb)O_6$ octahedra. The two- and three-coordinated O atoms are bonded to the (W,Nb) atoms with distances ranging from 1·89 to 2·24 Å. The same distribution of bond distances has been found in the compounds Li_2WO_4(III) (Wilhelmi, Waltersson & Löfgren, 1977) and Ag_2WO_4 (Skarstad & Geller, 1975), both having structures containing this kind of M_4O_{16} tetramer. The short O—O distances (2·51–2·64 Å) appear as shared edges, which is normal with most transition-metal-anion polyhedra involved in such types of linking in accordance with one of Pauling's

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* JCPDS Diffraction File No. 35-1498. See also deposition footnote.

* Lists of structure factors and the indexed powder pattern have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39781 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Positional and thermal parameters*

Standard deviations are given within parentheses.

	x	y	z	Occupancy	U_{11} or U(Å^2)
W,Nb(1)	0·18485 (7)	0·42083 (7)	−0·00123 (11)	0·955 (4)	0·0045 (2)
W,Nb(2)	0·23501 (7)	0·82954 (7)	0·20831 (11)	0·949 (4)	0·0058 (2)
Li(1)	0·1028 (51)	0·0438 (51)	0·7455 (78)	0·76 (9)	0·0145 (65)
Li(2)	0·9735 (42)	0·3256 (39)	0·4068 (65)	1	0·0174 (54)
Li(3)	0·5713 (44)	0·6405 (43)	0·4006 (68)	1	0·0201 (58)
Li(4)	0·5211 (58)	0·2133 (57)	0·2011 (89)	0·80 (10)	0·0226 (78)
O(1)	0·2089 (14)	0·3217 (14)	0·7050 (22)	1	0·0122 (18)
O(2)	0·2581 (14)	0·6632 (14)	0·9064 (22)	1	0·0114 (17)
O(3)	0·4346 (15)	0·8053 (15)	0·4223 (24)	1	0·0141 (19)
O(4)	0·0195 (14)	0·2174 (14)	0·0797 (21)	1	0·0110 (17)
O(5)	0·1360 (15)	0·9118 (15)	0·4415 (23)	1	0·0137 (19)
O(6)	0·6178 (16)	0·5824 (16)	0·7619 (25)	1	0·0173 (22)
O(7)	0·6888 (15)	−0·0187 (15)	−0·0351 (24)	1	0·0141 (19)
O(8)	0·9179 (14)	0·4348 (14)	0·7570 (21)	1	0·0106 (17)

	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W,Nb(1)	0·0061 (2)	0·0092 (3)	−0·0017 (2)	0·0016 (2)	0·0018 (2)
W,Nb(2)	0·0057 (2)	0·0069 (2)	−0·0024 (2)	0·0013 (2)	0·0008 (2)

Anisotropic thermal parameters are given in the form: $\exp\{-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})\}$.

Table 3. *Relevant interatomic distances in* Å

Standard deviations are given within parentheses.

(W,Nb)(1)–O(6′)	1·78 (1)	(W,Nb)(2)–O(7′)	1·78 (1)
–O(1)	1·80 (1)	–O(3)	1·79 (1)
–O(4)	1·89 (1)	–O(5)	1·80 (1)
–O(2)	1·92 (1)	–O(2)	2·11 (1)
–O(8′)	2·13 (1)	–O(8′)	2·12 (1)
–O(8)	2·24 (1)	–O(4′)	2·17 (1)
Li(1)–O(5)	2·00 (4)	Li(2)–O(4)	2·06 (3)
–O(7′)	2·03 (4)	–O(5′)	2·07 (3)
–O(5′)	2·05 (4)	–O(8′)	2·11 (3)
–O(1)	2·13 (4)	–O(1)	2·16 (3)
–O(4′)	2·30 (4)	–O(2′)	2·19 (3)
–O(4)	2·52 (4)	–O(8)	2·21 (3)
Li(3)–O(1′)	1·91 (4)	Li(4)–O(7′)	1·94 (5)
–O(3)	1·91 (3)	–O(3′)	1·95 (5)
–O(6)	1·94 (4)	–O(2′)	1·97 (5)
–O(6′)	1·99 (4)	–O(6′)	2·20 (4)
(W,Nb)(1)–W,Nb(2)	3·240 (1)	Li(3)–Li(4′)	2·71 (6)
–W,Nb(2′)	3·299 (1)	Li(2)–Li(2′)	2·76 (6)
–W,Nb(1′)	3·490 (2)	Li(2)–Li(1′)	2·83 (5)
		Li(2)–Li(1)	3·08 (5)

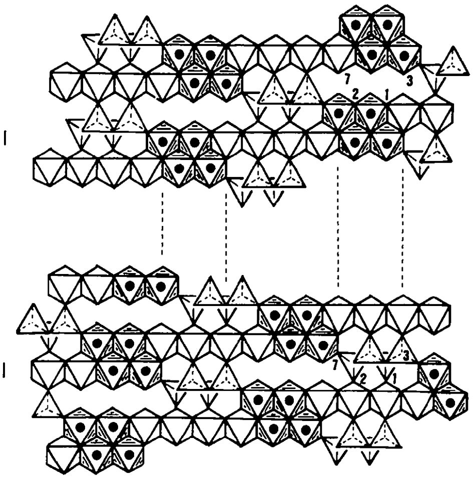

Fig. 1. Two consecutive layers of the idealized cubic close-packed structure of $Li_{2.09}W_{0.91}Nb_{0.09}O_4$. (I is the lower layer and II is the upper layer.) Filled circles represent (W,Nb). Empty octahedra and tetrahedra correspond to LiO_6 and LiO_4 polyhedra respectively. The Li atoms have been excluded for clarity. The numbers refer to some of the O atoms connecting the two layers shown.

rules (Pauling, 1960). The distortion of the oxygen lattice gives rise to elongated octahedral interstices containing two crystallographically independent Li atoms [Li(1) and Li(2)].

The Li(2)O_6 octahedron shows a relatively small scatter in Li(2)—O bond lengths (2·06–2·21 Å), although the O—O distances vary from 2·64 to 3·44 Å. In the Li(1)O_6 octahedron the Li atom is displaced from the centre so that four short (2·00–2·13 Å) and two long bonds (2·30 and 2·52 Å) arise. The coordination polyhedron may thus also be described as a very distorted tetrahedron. The O—O distances within this octahedron range from 2·70 to 3·39 Å.

The Li(3) and Li(4) atoms occupy tetrahedrally coordinated sites, and two of each kind form an Li_4O_{10} tetramer of edge-sharing tetrahedra. The Li—O distance-ranges within the tetrahedra are 1·91–1·99 Å and 1·94–2·20 Å, respectively. The O—O distances vary from 2·93 to 3·45 Å in the Li(3)O_4 and from 2·93 to 3·58 Å in the Li(4)O_4 tetrahedron. The longest distance corresponds to the outer edge of the tetramer, and the shorter distances are found between O atoms involved in edge-sharing.

Analogous kinds of elongated LiO_6 octahedra, with two long Li—O distances (2·30–2·58 Å), have been observed in several compounds with close-packed anion lattices, such as Li_2WO_4(II) (Waltersson, Werner &

Wilhelmi, 1977; Horiuchi, Morimoto & Yamaoka, 1979), Li_2WO_4(IV) (Horiuchi, Morimoto & Yamaoka, 1980) and L-$Li_2Mo_4O_{13}$ (Gatehouse & Miskin, 1974). A somewhat more regular LiO_6 octahedron appears in the hexagonally close-packed structure of $LiNb_3O_8$ (Lundberg, 1971), with Li—O distances between 2·08 and 2·34 Å.

The atomic distances within the LiO_4 tetrahedra are similar to those found in the structures of Li_2WO_4(II) and $Li_2W_2O_7$ (Okada, Morikawa, Marumo & Iwai, 1975), although the longest O—O distance, 3·58 Å, is rather long.

The metal-to-oxygen ratio of $Li_{2.09}W_{0.91}Nb_{0.09}O_4$ is very close to that of Li_2WO_4. At room temperature and atmospheric pressure the latter compound, called Li_2WO_4(I) (Zachariasen & Plettinger, 1961), adopts the phenacite structure type (Be_2SiO_4). The O atoms are spaciously arranged, and both Li and W are tetrahedrally coordinated.

Through exchange of small amounts of tungsten for niobium, as is the case in the present compound, a distorted close-packed array of O atoms is obtained. Close-packing of O atoms in Li_2WO_4 can also be achieved by increasing the pressure and temperature.

Three high-pressure phases have been found, of which Li_2WO_4(II) has a structure built up of cubic close-packed O atoms with the Li atoms octahedrally and tetrahedrally coordinated. Li_4O_{12} rings of corner-sharing LiO_4 tetrahedra and LiO_6 octahedra connect the W_4O_{16} groups of edge-sharing WO_6 octahedra into a three-dimensional framework.

The structures of Li_2WO_4(III) (Wilhelmi *et al.*, 1977) and Li_2WO_4(IV) (Horiuchi *et al.*, 1980) are both based on a hexagonally close-packed oxygen network, but the metal atoms are distributed in different manners. A complete structure determination of Li_2WO_4(III) has not been reported, although Wilhelmi *et al.* determined the tungsten–oxygen arrangement. The W atoms are located in octahedral interstices ordered in such a way that four WO_6 octahedra share edges and form W_4O_{16} groups, of a type different from those in Li_2WO_4(II), however.

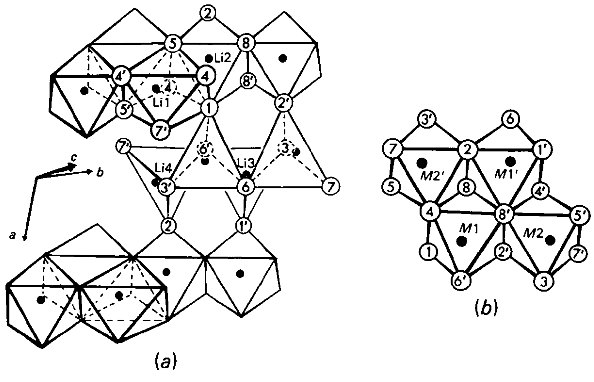

Fig. 2. (*a*) The framework of Li—O polyhedra and (*b*) the $(W,Nb)_4O_{16}$ group viewed perpendicular to the close-packed oxygen layers.

Table 4. *Experimental conditions and oxygen packing in the* Li_2WO_4 *polymorphs and* $Li_{2.09}W_{0.91}Nb_{0.09}O_4$

Compound	P(GPa)	T(K)	Oxygen arrangement	V(Å^3)/O
Li_2WO_4 (I) (Zachariasen & Plettinger, 1961)	~10^{-4}	775	Phenacite-type	23·8
Li_2WO_4 (II) (Horiuchi *et al.*, 1979)	0·3	900	c.c.p.	18·8
Li_2WO_4 (III) (Wilhelmi *et al.*, 1977)	2	1375→920	h.c.p.	18·6
Li_2WO_4 (IV) (Horiuchi *et al.*, 1980)	4	1125	h.c.p.	18·1
$Li_{2.09}$(W,Nb)O_4 (present work)	~10^{-4}	1175	c.c.p.	19·0

In the structure of Li_2WO_4(IV) the WO_6 octahedra are joined by edge-sharing to form infinite zigzag strings as in the orthorhombic form of PbO_2. The Li atoms exclusively occupy octahedral sites so that two-dimensionally infinite sheets of edge-sharing distorted LiO_6 octahedra are formed. The sheets are joined by the zigzag strings of WO_6 octahedra.

In spite of the similarities between $Li_{2.09}W_{0.91}Nb_{0.09}O_4$ and Li_2WO_4(II) with respect to the c.c.p. oxygen network and the type of coordination polyhedra surrounding the metal atoms, the modes of coupling of the LiO_4 tetrahedra to Li_4O_{10} and Li_4O_{12} tetramers, respectively, are of different kinds. The W_4O_{16} tetramers are also different. However, the W_4O_{16} group in $Li_{2.09}W_{0.91}Nb_{0.09}O_4$ can be recognized in Li_2WO_4(III).

As can be seen in Table 4, the density of the oxygen packing is increased by applying high pressure on Li_2WO_4(I) of phenacite structure type. It is interesting to note that a close-packed oxygen arrangement can also be obtained when a small amount of tungsten is replaced by the same amount of niobium.

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Structure of Metastable Lead Metavanadates: the Monoclinic PbV_2O_6(II) Modification

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Abstract. $M_r = 405\cdot07$, monoclinic, $C2/m$, $a = 15\cdot525\,(2)$, $b = 3\cdot6960\,(6)$, $c = 9\cdot436\,(4)$ Å, $\beta = 110\cdot44\,(1)^\circ$, $V = 507\cdot3\,(2)$ Å^3, $Z = 4$, $D_x = 5\cdot30$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot71069$ Å, $\mu = 36\cdot75$ mm^{-1}, $F(000) = 704$, $T = 293$ K; final $R = 0\cdot046$ for 313 observed reflections. All the atoms lie on mirror planes. The structure of PbV_2O_6(II) differs from that of other MX_2O_6 systems and consists of columns of double chains of edge-sharing VO_5 square pyramids which extend infinitely along the b axis; Pb atoms are interspersed.

Introduction. Recent studies on the equimolar $PbO.V_2O_5$ system (Calestani, Montenero, Pigoli & Bettinelli, 1984) show the existence of two new lead metavanadate phases, which crystallize from the melt when the cooling rate is extremely high; they are imbedded in a vitreous matrix. These phases, indicated as PbV_2O_6(II) and (III), are metastable at room temperature and present structures which differ from that of all other MX_2O_6 systems. Both transform on heating to the well known stable phase PbV_2O_6(I) (Jordan & Calvo, 1974) and must be considered as an intermediate lattice arrangement between the stable form and the glass.

The crystal-structure analysis of these compounds is therefore quite interesting for the comprehension of the structural evolution leading to the vitreous state. We present here the structural study of PbV_2O_6(II), *i.e.* of the first step of this transition between the ordered and disordered state.

Experimental. PbV_2O_6(II) can be obtained imbedded in a vitreous matrix by quenching near equimolar $PbO.V_2O_5$ melts on a steel vessel. Because of the tendency of the glass, at this cooling rate, to enrich itself in V_2O_5, the separation of crystalline PbV_2O_6(II) from the glass is followed by the formation of PbV_2O_7 (chervetite) for a V_2O_5/PbO molar ratio less than 1·2.

The separation of PbV_2O_6(II) single crystals from the quenched mass was quite difficult, since polycrystalline agglomerates appear, because of the high growth rate, as a compact mass in which the single components are practically indistinguishable. In spite of this, some small dark-brown crystals could be isolated by repeatedly breaking the samples.

Intensity data collected from a twin member of a small needle crystal ($0\cdot03 \times 0\cdot03 \times 0\cdot2$ mm), automated Philips PW 1100 four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation, 2–30° θ range, max. range h,k,l: 20,5,12, θ–2θ scan, 1·4° scan width, $0\cdot1^\circ$ s^{-1} scan rate; backgrounds estimated from 5 s counts at each end of scan. Lattice parameters determined by least-squares refinement of setting angles of 16 reflections in range $9 < \theta < 18^\circ$. One standard reflection (020), max. intensity variation 2·2%. 882 reflections measured of which 353 with $I > 3\sigma(I)$ considered observed and after correction for Lorentz and polarization effects resulted in 313 unique reflections, $R_{\text{int}} = 0\cdot042$. The strong high-$\chi$ (~90°) 002 and 004 reflections were not included in the list because of overlap with reflections from other twins. The absorption correction performed by the ψ-scan method (North, Phillips & Mathews, 1968) was affected by the same phenomenon and therefore was not utilized in the structure analysis. All calculations performed on a Gould SEL 32/77 computer using a local version of *SHELX76* (Sheldrick, 1976). Structure solved by