

## High-Pressure Synthesis and Structure of the New Niobium Phosphide Nb<sub>2</sub>P<sub>5</sub>

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### Abstract

Nb<sub>2</sub>P<sub>5</sub> was prepared by reaction of the elements at 3–5 GPa and 1273 K using a cubic-anvil-type apparatus. The crystal is orthorhombic, *Pnma*, with  $a = 16.742(3)$ ,  $b = 3.3499(6)$ ,  $c = 7.912(1)$  Å,  $Z = 4$ , and  $D_x = 5.10$  Mg m<sup>-3</sup>. The structure was refined to  $R = 0.037$  for 1198 independent reflections. The structure of Nb<sub>2</sub>P<sub>5</sub> is closely related to the OsGe<sub>2</sub>-type structure. Zigzag P<sub>∞</sub> chains are additionally inserted along the  $b$  axis between the Os<sub>2</sub>Ge<sub>4</sub> rhombic prisms of the OsGe<sub>2</sub>-type structure. Nb<sub>2</sub>P<sub>5</sub> is a metallic conductor and shows Pauli paramagnetism.

### Introduction

Recently we reported the preparation of FeP<sub>4</sub> at high pressures and its crystal structure (Sugitani, Kinomura, Koizumi & Kume, 1978). As shown by this experiment, use of high-pressure synthesis is very advantageous for producing a new phosphide with a high P content and for growing crystals suitable for structural analysis.

Transition-metal dipnictides are classified into two groups according to their coordination number. One structural family is the low-coordination structure for the late (Group VIII) transition-metal dipnictides and the other is the high-coordination structure for the early (Groups IV to VII) transition-metal dipnictides (Jeitschko & Donohue, 1973). Jeitschko & Donohue described the low-coordination structures as being represented by compounds with the marcasite, pyrite, arsenopyrite, PdP<sub>2</sub> and related structures in which the transition-metal atoms are coordinated by six pnictogen atoms or less, and dipnictides with OsGe<sub>2</sub>, PbCl<sub>2</sub>, MoP<sub>2</sub>, TiS<sub>2</sub> and CuAl<sub>2</sub>-type structures as belonging to the family with high-coordination structures where the coordination number of the transition-metal atoms was higher than that in low-coordination structures. The near-neighbor environments of both metal and pnictogen in high-coordination structures show no sharp

distinction between nearest and second-nearest neighbors. When the ratio of metal to nonmetal elements increases, generally the compounds with the low-coordination structure are produced. In such a compound with high P content, P atoms tend to bond to each other, and the directional-bonding character of P is predominant. The transition-metal phosphides CrP<sub>4</sub>, MoP<sub>4</sub> (Jeitschko & Donohue, 1972) and VP<sub>4</sub> (Kanno, Kinomura & Koizumi, 1979) are examples of such compounds.

In the Nb–P system, the dipnictide NbP<sub>2</sub> which was prepared under ambient pressure has been the compound with the highest P content and its structure is known to be the OsGe<sub>2</sub> type with a high coordination number (Hulliger, 1964). Another niobium phosphide with a defect PbFCl-type structure, NbP<sub>1.75</sub>, was prepared at high pressure (Jeitschko, Donohue & Johnson, 1976). This compound is also a high-coordination compound. A new niobium phosphide with a higher P content, Nb<sub>2</sub>P<sub>5</sub>, has been synthesized and its structure and properties are presented in this paper.

### Sample preparation and experimental

Powdered Nb metal (99.9% purity) and red P (Merck, 98% purity) were used as starting materials. They were mixed with a Nb/P ratio between 1:3 and 1:6. With a cubic-anvil-type high-pressure apparatus, the samples, which were contained in boron nitride crucibles, were subjected to the high-temperature–high-pressure conditions of 1273–1323 K and 3–5 GPa. After the desired conditions had been maintained for 0.5 h, the samples were quenched to room temperature before the pressure was released. The product was found (from its X-ray powder pattern) to be a mixture of a new niobium phosphide and black P. The black P formed as a by-product was dissolved by HNO<sub>3</sub> solution.

Single crystals (~50 μm in diameter and ~60 μm in length) of this new niobium phosphide were prepared from the starting material with a metal-to-phosphorus

ratio of 1:6. The starting material was heated at 3.5 GPa and 1273 K, held at this temperature for 3 h, slowly cooled over 2 h to 1173 K and quenched.

### Characterization

Chemical analysis gave a Nb content of 54.6 wt%, as compared with 54.54 wt% calculated for Nb<sub>2</sub>P<sub>5</sub>.

Electrical-resistivity measurements were carried out from 77 K to room temperature using a four-probe technique on pellet-form specimens ~6 mm in diameter and ~4 mm in length pressed at room temperature and 5 GPa. Metallic conductivity was found for Nb<sub>2</sub>P<sub>5</sub>;  $\rho_{273\text{K}} = 1.22 \times 10^{-3}$ ,  $\rho_{77\text{K}} = 8.2 \times 10^{-4}$   $\Omega$  m.

The magnetic susceptibility of this phosphide measured by a conventional Faraday balance was very weak and did not depend on temperature within the range from 77 K to room temperature.

The new compound Nb<sub>2</sub>P<sub>5</sub> decomposed to NbP<sub>2</sub> and elemental P on heating in an evacuated silica tube at 1073 K for 12 h. This indicates that Nb<sub>2</sub>P<sub>5</sub> is stable only at high pressures.

### Structure determination

Single crystals of Nb<sub>2</sub>P<sub>5</sub> were investigated with Weissenberg and Buerger precession cameras using Co K $\alpha$  radiation. The diffraction patterns could be indexed with an orthorhombic unit cell. The orthorhombic cell dimensions were determined to be  $a = 16.742$  (3),  $b = 3.3499$  (6),  $c = 7.912$  (1) Å by a least-squares refinement using 36 reflections measured with a four-circle diffractometer.

Diffraction extinctions ( $0kl$  present only with  $k + l = 2n$ ,  $hk0$  only with  $h = 2n$ ) were characteristic of space groups  $Pnma$  or  $Pn2_1a$ ;  $Pnma$  was found to be correct during the structure determination.

The observed density of 5.08 Mg m<sup>-3</sup> was in good agreement with that calculated (5.099 Mg m<sup>-3</sup>) with four formula units per cell.

The crystal used for the collection of the three-dimensional intensity data was an irregular equidimensional fragment ~60  $\mu$ m in diameter. Graphite-monochromated Mo K $\alpha$  radiation was used on a Rigaku automatic four-circle diffractometer. The  $\omega$ - $2\theta$  scan technique was used; the scan speed was 2° (2 $\theta$ ) min<sup>-1</sup> and the background was counted for 20 s at both ends of each scan. All reflections within the hemisphere up to  $(\sin \theta)/\lambda = 0.9$  Å<sup>-1</sup> were collected. A Lorentz-polarization correction was made, but an absorption correction was not applied because of the small size of the crystal.

The three-dimensional Patterson synthesis revealed the approximate positions of the Nb atom pair. The structure was refined with a block-diagonal least-

Table 1. Atomic positional and thermal ( $\times 10^3$ ) parameters

The e.s.d.'s are given in parentheses in units of the last decimal place.

	x	y	z	$U_{\text{eq}}$ (Å <sup>2</sup> )
Nb(1)	0.09506 (2)	0.25	0.16391 (6)	29
Nb(2)	0.27343 (3)	0.25	0.17210 (6)	31
P(1)	0.04016 (8)	0.25	0.46144 (17)	47
P(2)	0.38426 (8)	0.75	0.18293 (17)	48
P(3)	-0.02257 (8)	0.75	0.12131 (18)	47
P(4)	0.31556 (8)	0.25	0.49344 (18)	53
P(5)	0.18504 (8)	0.75	0.34794 (17)	53

squares program. Atomic scattering factors for Nb<sup>5+</sup> and P atoms and a dispersion correction were taken from *International Tables for X-ray Crystallography* (1974).

Refinement with anisotropic temperature factors resulted in  $R = \sum (|F_o| - |F_c|) / \sum |F_o| = 0.0402$  and  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.0507$  for 1208 unique reflections. The final  $R$  value was 0.0367 and  $R_w$  was 0.0448 for 1198 reflections, excluding the ten strong reflections most severely affected by secondary extinction. The weighting scheme was  $w = 1/[\sigma^2(F_o) + 0.0005|F_o|^2]$ , where  $\sigma$  is the standard deviation in  $F_o$ . Observed structure factors which were smaller than three times the standard deviations were excluded from the calculation.\* The final positional and thermal parameters are listed in Table 1.

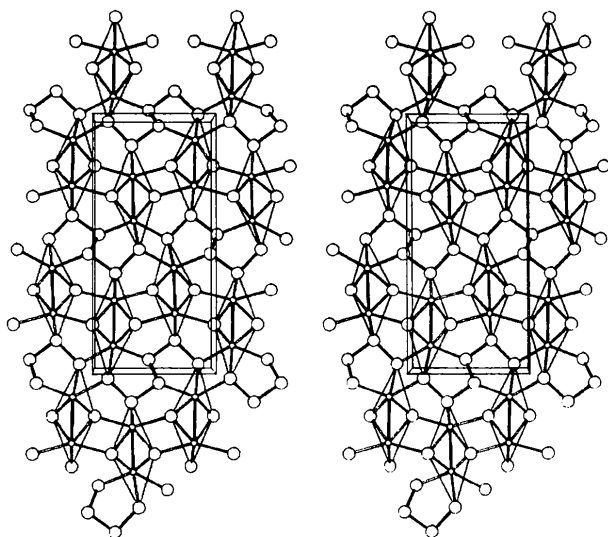
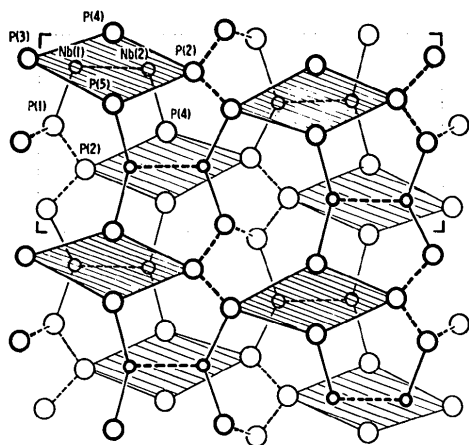
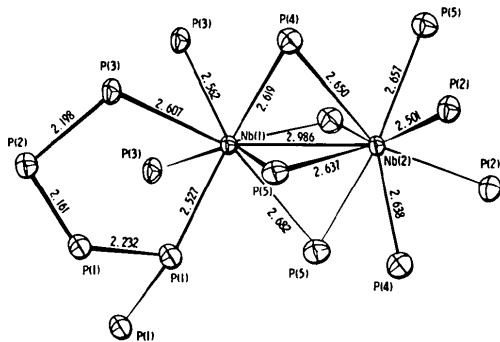
Computations were carried out on a FACOM 270/20 computer of Kwansai Gakuin University with programs developed by one of the authors (KN) and, for drawing the thermal ellipsoids and the stereodiagram, by A. Takenaka (private communication). Computations for the calculation of the interatomic distances and bond angles were carried out on an ACOS 900 computer of Osaka University with the program *UMBADTEA* (Finger, 1968).

### Discussion

The structure of Nb<sub>2</sub>P<sub>5</sub> is shown in Figs. 1 and 2, and the interatomic distances and bond angles are listed in Table 2. The nearest-neighbor environment of Nb<sub>2</sub>P<sub>5</sub> is given in Fig. 3.

For comparison, the NbP<sub>2</sub> structure, which is OsGe<sub>2</sub>-type, is shown projected on (010) in Fig. 4 (Hulliger, 1968). It can be seen that the structure of Nb<sub>2</sub>P<sub>5</sub> is closely related to that of NbP<sub>2</sub>. In these compounds, each metal atom is surrounded by eight P

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35366 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Fig. 1. Stereodrawing of the Nb<sub>2</sub>P<sub>5</sub> structure.Fig. 2. The Nb<sub>2</sub>P<sub>5</sub> structure projected on the (010) plane. Dashed lines indicate anion-anion and cation-cation bonds.Fig. 3. Nearest-neighbor environment in Nb<sub>2</sub>P<sub>5</sub>. Thermal ellipsoids are drawn to include the 99% probability level.Table 2. Interatomic distances (Å) and angles (°) in the Nb<sub>2</sub>P<sub>5</sub> structure

Standard deviations are in parentheses.

The superscripts refer to atoms in the following positions:

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

Nb(1)—Nb(2)	2.986 (1)	Nb(2)—Nb(1)	2.986 (1)
P(1)	2.527 (1)	P(2)	2.501 (1) × 2
P(3)	2.607 (1) × 2	P(4) <sup>ii</sup>	2.650 (1) × 2
P(3) <sup>i</sup>	2.562 (2)	P(5)	2.652 (1) × 2
P(4) <sup>ii</sup>	2.619 (1) × 2	P(4)	2.638 (2)
P(5)	2.682 (1) × 2	P(5) <sup>ii</sup>	2.657 (2)
P(1)—Nb(1)	2.527 (1)	P(4)—Nb(1) <sup>vi</sup>	2.619 (1) × 2
P(1) <sup>iii</sup>	2.232 (2) × 2	Nb(2) <sup>vi</sup>	2.650 (1) × 2
P(2) <sup>iv</sup>	2.161 (2)	Nb(2)	2.638 (2)
P(2)—Nb(2)	2.501 (1) × 2	P(5) <sup>iv</sup>	2.804 (2)
P(1) <sup>ii</sup>	2.161 (2)	P(5)	2.984 (2) × 2
P(3) <sup>v</sup>	2.198 (2)	P(5)—Nb(1)	2.682 (1) × 2
P(3)—Nb(1)	2.607 (1) × 2	Nb(2)	2.632 (1) × 2
Nb(1) <sup>viii</sup>	2.562 (2)	Nb(2) <sup>vii</sup>	2.657 (2)
P(2) <sup>vii</sup>	2.198 (2)	P(4) <sup>ii</sup>	2.804 (2)
P(3) <sup>i</sup>	2.657 (2) × 2	P(4)	2.984 (2) × 2

Nb(1)—P(1)—P(1) <sup>iii</sup>	118.27 (7) × 2
Nb(1)—P(1)—P(2) <sup>iv</sup>	122.84 (7)
P(1) <sup>iii</sup> —P(1)—P(1) <sup>ix</sup>	97.20 (10)
P(1) <sup>iii</sup> —P(1)—P(2) <sup>iv</sup>	97.53 (8) × 2
Nb(2)—P(2)—Nb(2) <sup>x</sup>	84.08 (5)
Nb(2)—P(2)—P(1) <sup>ii</sup>	113.99 (5) × 2
Nb(2)—P(2)—P(3) <sup>v</sup>	123.41 (5) × 2
P(1) <sup>ii</sup> —P(2)—P(3) <sup>v</sup>	98.97 (8)
Nb(1)—P(3)—Nb(1) <sup>x</sup>	79.95 (4)
Nb(1)—P(3)—Nb(1) <sup>viii</sup>	118.14 (4) × 2
Nb(1)—P(3)—P(2) <sup>vii</sup>	116.42 (5) × 2
Nb(1) <sup>viii</sup> —P(3)—P(2) <sup>vii</sup>	106.53 (6)
Nb(1) <sup>iv</sup> —P(4)—Nb(1) <sup>vi</sup>	79.48 (4)
Nb(2) <sup>iv</sup> —P(4)—Nb(2) <sup>vi</sup>	78.40 (4)
Nb(1) <sup>iv</sup> —P(4)—Nb(2) <sup>iv</sup>	69.05 (3) × 2
Nb(1) <sup>iv</sup> —P(4)—Nb(2)	130.45 (4) × 2
Nb(2) <sup>iv</sup> —P(4)—Nb(2)	111.33 (4) × 2
Nb(1)—P(5)—Nb(1) <sup>x</sup>	77.28 (4)
Nb(2)—P(5)—Nb(2) <sup>x</sup>	79.02 (4)
Nb(1)—P(5)—Nb(2)	68.38 (3) × 2
Nb(1)—P(5)—Nb(2) <sup>vi</sup>	132.13 (4) × 2
Nb(2)—P(5)—Nb(2) <sup>vi</sup>	111.28 (4) × 2

atoms, six of which form a trigonal prism with two more P atoms outside the rectangular faces. The trigonal prisms are paired by sharing one of the three rectangular faces and piled up along the *b* axis by sharing the triangular faces, thus forming infinite rhombic prisms with the composition Nb<sub>2</sub>P<sub>4</sub>. These rhombic prisms are connected to each other through Nb—P as well as P—P bonds. But in the Nb<sub>2</sub>P<sub>5</sub> structure, zigzag P<sub>∞</sub> chains enter the spaces which are surrounded by four rhombic prisms, so that the near neighbors of P atoms differ slightly from that of P

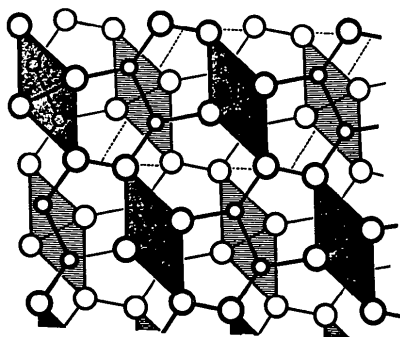


Fig. 4. Structure of  $\text{NbP}_2$  projected on the (010) plane.

atoms in the  $\text{NbP}_2$  structure, especially in the case of P(2) in  $\text{Nb}_2\text{P}_5$ . The Nb(1)–Nb(2) distance of 2.986 Å indicates the existence of Nb–Nb pairs in the structure. This distance is quite close to the distance of 3.00 Å for Nb–Nb pairs found in  $\text{NbAs}_2$  (Furuseth & Kjekshus, 1965). In addition to this Nb–Nb pair, Nb atoms located at the same crystallographic sites of adjacent unit cells are close to each other (not shown in Fig. 3), at a distance of  $b = 3.350$  Å through the triangular faces.

The P(1) atom is surrounded by three P atoms and one Nb atom. The P(1)–P(1) and P(2)–P(3) distances of 2.232 and 2.198 Å correspond well to the distances for full P–P single bonds observed in elemental P (2.23 Å for black P and 2.22 Å for Hittorf's P) (Brown & Rundqvist, 1965; Thurn & Krebs, 1969). Although the P(1)–P(2) distance of 2.161 Å is a little shorter than the standard values, it must also be considered as a full single P–P bond. The zigzag chains formed by the P(1) atoms in the  $\mathbf{b}$  direction are the most interesting features of this structure. The P(3)–P(3)<sup>I</sup>, P(4)<sup>II</sup>–P(5) and P(4)–P(5) distances of 2.657, 2.804 and 2.984 Å are much longer than the other P–P single-bond distances mentioned above.

Each of the P(4) and P(5) atoms is coordinated by five near Nb neighbors in a distorted square-pyramidal arrangement and this suggests  $sp^3d$  hybridization for each P atom. These P atoms correspond to the P(1) atom in  $\text{CrP}_2$  which also has five metal-atom neighbors forming a distorted square pyramid (Jeitschko & Donohue, 1973).

If only short near-neighbor Nb–P and P–P interactions are taken into account, there are 38/2 bonds per  $\text{Nb}_2\text{P}_5$  formula unit: 8/2 for each Nb(1) and Nb(2), 4/2 for each P(1), P(2) and P(3) and 5/2 for each P(4) and P(5) atom. A deficit of three electrons occurs for 35 valence electrons in  $\text{Nb}_2\text{P}_5$ , if two-electron bonds are assumed. In the high-coordination structures, it is generally difficult to distinguish between nearest and second-nearest neighbors because of the lack of a sharp distinction. In other words, weak, partial bonds, which cannot be considered as full bonds, are often observed. Such bonds as P(3)–P(3)<sup>I</sup>, P(4)<sup>II</sup>–P(5), P(4)–P(5),

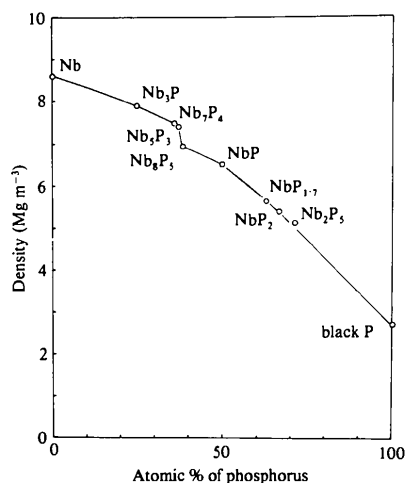


Fig. 5. Relation between density and atomic percentage of P in various kinds of niobium phosphides. These data are taken from recent reports:  $\text{Nb}_3\text{P}$ ,  $\text{NbP}_2$ ,  $\text{NbP}$  (Rundqvist, 1966a);  $\text{Nb}_7\text{P}_4$  (Rundqvist, 1966b);  $\text{Nb}_3\text{P}_3$  (Hassler, 1971);  $\text{Nb}_4\text{P}_5$  (Anugul, Pontchour & Rundqvist, 1973).

Nb(1)–Nb(1)<sup>x</sup> and Nb(2)–Nb(2)<sup>x</sup>, as well as Nb(1)–Nb(2) in  $\text{Nb}_2\text{P}_5$ , are weak bonds. These weak interactions make the structure even more electron deficient. A lack of bonding electrons is characteristic of metals and intermetallic compounds, so metallic conductivity and Pauli paramagnetism are indicated for this compound.

From the similarity of both structures and the near-neighbor environments in  $\text{OsGe}_2$  and  $\text{Nb}_2\text{P}_5$ , the structure of  $\text{Nb}_2\text{P}_5$  can also be assigned to a high-coordination structure. However, the existence of P(1), which forms a  $\text{P}_\infty$  chain and has an environment which is characteristic of the low-coordination structure, indicates that the structure of  $\text{Nb}_2\text{P}_5$  has features of both the low- and high-coordination structures, *i.e.* it is in the transitional state between the low- and high-coordination structures.

As shown by the result of annealing  $\text{Nb}_2\text{P}_5$  at ambient pressure, the mixture of  $\text{NbP}_2$  and elemental P is stable at low pressure. The density of the new high-pressure  $\text{Nb}_2\text{P}_5$  phase is compared in Fig. 5 with the densities of other Nb–P compounds. When the volumes of the mixture (black P was taken for elemental P) and  $\text{Nb}_2\text{P}_5$  are compared,  $\text{Nb}_2\text{P}_5$  is smaller in volume by about 1.8%. Although the volume change is not so large because of the structural similarity of both phosphides,  $\text{Nb}_2\text{P}_5$  shares a general feature of the high-pressure phases. In addition to P atoms which form trigonal prisms around Nb atoms, the zigzag  $\text{P}_\infty$  chains are inserted into the lattice as a result of the high-pressure conditions.

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## The Structure of V<sub>2</sub>GaO<sub>5</sub>

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### Abstract

Crystals of V<sub>2</sub>GaO<sub>5</sub> (V<sup>III</sup>V<sup>IV</sup>GaO<sub>5</sub>) are monoclinic, space group *C2/m*, with *Z* = 6, *a* = 17.758 (5), *b* = 2.990 (1), *c* = 9.323 (3) Å, β = 98.44 (2)°, *V* = 489.6 Å<sup>3</sup> and *d<sub>c</sub>* = 5.12 Mg m<sup>-3</sup>. Intensities for 605 reflexions, collected on a four-circle diffractometer, were used in the structure solution and the structure was refined to a final *R* value = 0.040 and *R<sub>w</sub>* = 0.055. It is built up from β-gallia-like columns containing all the gallium atoms and from chains of VO<sub>6</sub> octahedra with the direction parallel to the *c* axis. Layers generated from these alternate chains, linked by corner-shared polyhedra, pile up along the *b* axis.

### Introduction

Investigation of the ternary systems vanadium–metal–oxygen gave compounds containing vanadium in both oxidation states +3 and +4. These compounds were sintered at temperatures between 1273 and 1473 K under oxygen partial pressures ranging from 10<sup>-5</sup> to

10<sup>-12</sup> atm (1 to 10<sup>-7</sup> Pa) using techniques already described (Cros, 1976). Phase equilibria in the V<sub>2</sub>O<sub>3</sub>–VO<sub>2</sub>–Ga<sub>2</sub>O<sub>3</sub> system at 1273 K showed formation of the compound V<sub>6</sub>Ga<sub>2</sub>O<sub>13</sub> (V<sup>III</sup>V<sup>IV</sup>Ga<sub>2</sub>O<sub>13</sub>) or 2V<sub>3</sub>O<sub>5</sub>–Ga<sub>2</sub>O<sub>3</sub> (Cros, Caramel & Kerner-Czeskleba, 1977).

In more recent investigations at temperatures above 1423 K a new compound containing vanadium(III) and (IV) and gallium could be prepared for the ratio V/Ga = 2 and with formula V<sub>2</sub>GaO<sub>5</sub> (V<sup>III</sup>V<sup>IV</sup>GaO<sub>5</sub>) or V<sub>4</sub>O<sub>7</sub>–Ga<sub>2</sub>O<sub>3</sub> (Cros, in preparation).

These mixed oxides, although containing vanadium(III), are very stable in air at room temperature. Until now, single crystals have only been obtained for the V<sub>2</sub>GaO<sub>5</sub> compound; its structure will be described in this paper.

### Experimental

Single crystals of V<sub>2</sub>GaO<sub>5</sub> used for the crystallographic study were obtained at 1423 K in the presence of iodine in a quartz tube sealed under primary