

sont les seules entre lesquelles n'existent que des liaisons hydrogènes, c'est aussi selon le plan (001) que se produit un clivage très facile, (iii) toutes les formes que nous avons observées sur ces cristaux, à savoir la bipyramide {111}, le prisme {110} et les pinacoïdes {100}, {010}, {001}, sont composées de faces  $F$ , (iv) le paramètre de la rangée [110] de  $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O} \alpha$  est très voisin du double paramètre de la rangée [110] de  $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O} \beta$ :  $[110]_\alpha = 5,08$ ;  $2[110]_\beta = 5,20 \text{ \AA}$ ; en plus les épaisseurs des couches ( $d_{220}$ ) $_\alpha = 4,81$  et ( $d_{110}$ ) $_\beta = 5,16 \text{ \AA}$  ont des valeurs proches; enfin la comparaison des p.b.c.  $\langle 110 \rangle$  figurant dans deux couches respectives  $d_{220}$  et  $d_{110}$  des espèces  $\alpha$  et  $\beta$  révèle entre chacun d'eux une similitude remarquable des positions relatives de tous les groupements  $\text{NO}_3^-$ , des atomes de calcium et des trois quarts des oxygènes des molécules d'eau. Cette analogie structurale peut être à l'origine de la croissance orientée de cristaux de  $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O} \alpha$  par rapport à la matrice des cristaux de  $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O} \beta$  au dépend desquels ils se développent.

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## High-Pressure Phases with Ordered Defect PbFCl Type Structures in the Systems V–P and Nb–P

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The new compounds  $\text{VP}_{1.75}$  and  $\text{NbP}_{1.7}$  were prepared from the elemental components at pressures of 35–55 kbar. They are metallic conductors and crystallize with PbFCl type subcells. The structure of  $\text{VP}_{1.75}$  was determined from single-crystal counter data and refined to an  $R$  of 0.044 for 788 independent structure factors. The space group is  $P4m2$  with  $a = 6.3237(4)$ ,  $c = 7.2671(7) \text{ \AA}$ ,  $Z = 8$ . The superstructure arises from the ordered arrangement of vacancies on the F site of the PbFCl type subcell. Some P positions were found with partial occupancies and a model for further short-range order is proposed on the basis of an analysis of the P–P bonding.

### Introduction

The P-rich section of the systems V–P and Nb–P has been repeatedly investigated under pressures no higher than can be sustained in unsupported hot quartz tubes

(Chêne, 1941; Zumbusch, Biltz, Reinecke & Wiechmann, 1942; Schäfer & Fuhr, 1965). These reports agree on the existence of the phases VP, NbP,  $\text{VP}_2$ , and  $\text{NbP}_2$ . No indications for compounds with compositions between the mono- and the diphosphide were found. We have investigated these systems at high pressure and, in addition to the ambient pressure compounds, we found phases with intermediate composition which are described here.

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### Synthesis, properties, and cell dimensions

High-purity powders of V, Nb, and red P were intimately mixed in metal:P ratios between 3:4 and 1:3. Cold-pressed pellets of these mixtures were placed in boron nitride crucibles, surrounded by a graphite-sleeve heater which was inserted in a pyrophyllite tetrahedron. Temperature was measured with a Pt-Pt/Rh thermocouple placed at the surface of the cylindrical graphite-sleeve heater. Pressure of 35 to 55 kbar was applied with a tetrahedral anvil press. Detailed operating procedures have been described by Bither, Gillson & Young (1966).

Because of temperature gradients in the cylindrical samples, the reaction products generally consisted of several phases of which the low-pressure compounds  $VP_2$  (Hulliger, 1964), NbP (Boller & Parthé, 1963), and  $NbP_2$  (Rundqvist, 1966a) were identified through their powder patterns. In samples with a V:P ratio of 1:2.5 excess black P was observed, indicating the absence of high-pressure compounds with compositions similar to  $CrP_4$  (Jeitschko & Donohue, 1972) and  $MnP_4$  (Jeitschko & Donohue, 1975).

The largest crystals of the new high-pressure compounds were isolated from samples with initial metal:P ratios between 2:3 and 1:2. The samples were heated under 55 kbar to 1250°C, held at that temperature for 2h, slowly cooled within 2h to 1100°C, and quenched while still under pressure. They were kept at ambient conditions in open containers for several years without decomposing or oxidizing.

Large, black, brittle crystals of the new compounds were isolated from the samples. They were identified through their X-ray powder patterns. Electrical conductivity measurements on single crystals of unknown orientation with the four-probe technique indicated metallic behavior. The new phase in the V-P system had resistivities of  $\rho_{298K} = 2 \times 10^{-4}$  and  $\rho_{4.2K} = 7 \times 10^{-5}$  ohm cm. The corresponding values for a crystal of the new phase in the Nb-P system were  $\rho_{298K} = 3 \times 10^{-2}$  and  $\rho_{4.2K} = 1 \times 10^{-2}$  ohm cm. Variation of the conductivity with composition was not investigated.

X-ray powder patterns of the ground samples are characteristic of a PbFCl type structure as found for instance for NbSiAs (Johnson & Jeitschko, 1973). Lattice constants for this tetragonal cell, which later proved to be only a subcell, were refined from Guinier-Hägg data with high-purity KCl ( $a = 6.2931$  Å) as standard. They are  $a = 3.1618$  (2),  $c = 7.2671$  (7) Å for this phase in the V-P system, and  $a = 3.3396$  (4),  $c = 7.649$  (1) Å for the corresponding phase in the Nb-P system. The standard deviations (in parentheses) are those of the least-squares refinements and do not reflect compositional variations in lattice constants. Samples prepared in other high-pressure experiments showed variations in lattice constants of up to ten times those of the above given standard deviations. A systematic study of the homogeneity ranges, however, was not intended.

The chemical composition of the new phases was indicated by the synthesis experiments to lie between the mono- and the diphosphide. The structure determination of the vanadium phosphide resulted in a composition  $VP_{1.75}$ . Its density, measured by displacement in bromoform, was 4.87, calculated density 4.80 g/cm<sup>3</sup>. Chemical analysis of the corresponding phase in the Nb-P system suggested a composition  $NbP_{1.6 \pm 0.1}$ . Its measured density was 5.65 g/cm<sup>3</sup>. This corresponds to a composition of  $NbP_{1.69}$  assuming partial occupancy of P sites and full occupancy of the metal positions. We will refer to this phase subsequently as  $NbP_{1.7}$ .

Weak superstructure lines were observed in the powder pattern of  $VP_{1.75}$  which required doubling of  $a$ . Thus the tetragonal cell dimensions of  $VP_{1.75}$  are  $a = 6.3237$  (4),  $c = 7.2671$  (7) Å,  $V = 290.60$  (4) Å<sup>3</sup>. They were confirmed in the single-crystal study.

Buerger precession photographs of  $NbP_{1.7}$  also showed a superstructure in long-exposure films, which at first suggested a five times larger  $a$ . Further examination, however, revealed a large number of systematic non-space-group extinctions suggesting twinning (Fig. 1). All reflections were accounted for by a tetragonal cell of Laue symmetry  $4/mmm$  with  $a = 7.468$  (1),  $c = 7.649$  (1) Å which has a  $\sqrt{5}$  times larger  $a$  axis than the PbFCl-like subcell. A similar relationship between a tetragonal subcell and a tetragonal superstructure is known for scheelite-related structures (Sillén & Sundvall, 1943), for  $MoNi_4$  (Harker, 1944), for  $Ti_2Ga_3$  (Pötzschke & Schubert, 1962), and for  $La_4Re_2O_{11}$  (Lagervall, Löfgren, Waltersson & Wilhelmi, 1975).

The superstructure of  $VP_{1.75}$  was observed in powder photographs shortly after the samples were prepared and the same superstructure reflections were recorded after the samples had been stored for several years. The superstructure reflections in  $NbP_{1.7}$  are much weaker and were observed only in single-crystal photographs taken eight years after the samples were prepared. It is not known whether the long equilibrating time is necessary to develop long-range order in  $NbP_{1.7}$ .

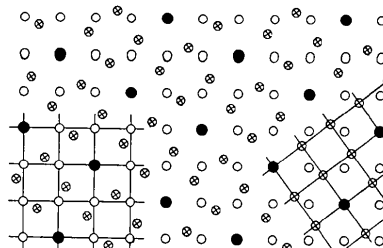


Fig. 1. Reciprocal lattice planes  $hkl$  ( $l=0$ , or 1, or 2, etc.) of a twin of  $NbP_{1.7}$ . Black dots represent strong reflections corresponding to the PbFCl type subcell. Open circles and crossed circles represent the two twin orientations of the superstructure.

Crystal structure of  $VP_{1.75}$ 

## Space group

Precession photographs of  $VP_{1.75}$  single crystals showed  $4/mmm$  symmetry and were indexed with the cell given above. No systematic absences of reflections were observed. Intensity calculations for the pronounced PbFCl type subcell gave good agreement between calculated and observed intensities. Therefore the space group for the large cell had to be a subgroup of  $P4/mmm$ , the space group of the PbFCl type structure. Of those (Neubüser & Wondratschek, 1966) only  $P4mm$  and  $P\bar{4}m2$  are compatible with the characteristics of the precession patterns. The structure was successfully refined in  $P\bar{4}m2$  and the distribution of completely vacant and fully occupied P positions clearly excludes space group  $P4mm$ . No indications for twinning were observed in back-reflection Weissenberg photographs.

## Intensity data

The single crystal of  $VP_{1.75}$  used for the structure determination had the shape of a triangular prism with a cross-section of  $0.15 \times 0.33 \times 0.33$  mm and a height of 0.05 mm. It was mounted in an automated four-circle Picker diffractometer at random orientation to minimize the chances of multiple reflection. For the purpose of the absorption correction, however, the orientation was subsequently well determined. Intensities were measured with Zr-filtered Mo-radiation, scintillation counter and pulse-height discriminator. Scans were along  $2\theta$  with a speed of  $0.5^\circ 2\theta/\text{min}$  and a scan angle of  $1.5^\circ 2\theta$  plus the angular separation of the  $K\alpha$  doublet. Background was counted for 20 s at both sides of each peak. All reflections within one octant up to  $75^\circ 2\theta$  were measured. Absorption was corrected for by a program by Prewitt (1967), as described by Wuensch & Prewitt (1965). Transmission values varied between 0.57 and 0.80.

## Structure refinements and determination of the superstructure

The very pronounced PbFCl type subcell of  $VP_{1.75}$

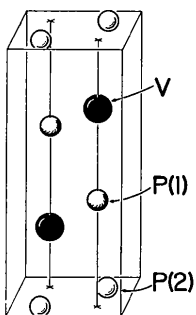


Fig. 2. PbFCl-type subcell of  $VP_{1.75}$ . Atom designations correspond to those of Table 1. The superstructure arises through the ordered arrangement of vacant, partially, and fully occupied P(2) positions as shown in Fig. 3.

(Fig. 2) was recognized at an early stage of our investigation and was refined first. A full-matrix least-squares program (Finger, 1969) was used with scattering factors for neutral atoms (Cromer & Mann, 1968) corrected for anomalous dispersion (Cromer & Liberman, 1970). Large thermal parameters for the P(2) position (which corresponds to the F site in PbFCl) indicated partial occupancy.

Refinement of occupancy factors and isotropic thermal parameters (Table 1) resulted in an  $R$  of 0.089 for 254 subcell reflections. Since the thermal parameter of the P(2) position was still very high, anisotropic thermal parameters were introduced. These showed that the P(2) atoms were displaced from their ideal positions mainly in the plane perpendicular to  $c$ .  $R$  for this refinement was 0.043 for the same number of subcell reflections.

Table 1. Results of the refinement of the  $VP_{1.75}$  subcell with defect PbFCl type structure (space group  $P4/nmm$ , origin at center)

	Position	$x$	$y$	$z$	Occupancy	$B$ ( $\text{\AA}^2$ )
V	2(c)	$\frac{1}{2}$	$\frac{1}{2}$	0.2580 (2)	1	0.52 (4)
P(1)	2(c)	$\frac{1}{4}$	$\frac{1}{4}$	0.6032 (3)	1	0.61 (5)
P(2)	2(a)	$\frac{1}{4}$	$\frac{3}{4}$	0	0.75 (1)	2.2 (1)

For the determination of the superstructure, least-squares refinements were carried out initially in both possible space groups ( $P4mm$  and  $P\bar{4}m2$ ) varying occupancy factors for those P positions which correspond to P(2) of the subcell. Only the refinement in  $P\bar{4}m2$  converged and a pattern of occupied, partially occupied, and empty P positions emerged. This was sufficient to phase a difference synthesis for the superstructure using a program by Fritchie & Guggenberger (1967). It showed that the partially occupied P sites are better described with 'split' atoms (Fig. 3). In subsequent least-squares refinements a parameter for secondary extinction was varied according to Zachariasen's (1963) approximation  $I_{\text{corr}} = I_{\text{uncorr}} / (1 - cI_{\text{uncorr}})$ , where  $c$  refined to  $0.31 \times 10^{-5}$ . The occupancy factors for the P positions corresponding to the P(2) positions of the subcell were all refined. Those which correspond to the crosses of Fig. 2 were found with an occupancy factor of  $-0.008 \pm 0.009$ , and those which correspond to the black dots had an occupancy factor of  $0.994 \pm 0.009$ . In the final refinements these occupancy factors were held fixed at 0 and 1 respectively.

Simultaneous refinement of occupancy and isotropic thermal parameters of P(4) and P(5) led to somewhat low thermal parameters (0.08 and  $0.33 \text{\AA}^2$  respectively), and we preferred to hold both these parameters at  $B=0.4 \text{\AA}^2$  in the final refinements (Table 2) to obtain more reliable occupancy factors. However, the interactions between the thermal and occupational parameters were not serious: the overall composition obtained in the final refinement corresponds to  $VP_{1.746}$ , while compositions  $VP_{1.729}$  and  $VP_{1.772}$  were calculated

from refinements where the  $B$  values of those P atoms were held at 0.2 and 0.7 Å<sup>2</sup>, respectively. Those  $B$  values were judged as the lower and upper acceptable limits, especially when compared to the  $B$  values of the other atoms in this and similar compounds. Refinements of occupancy parameters of P(1) and P(2) together with their thermal parameters resulted in occupancies of  $0.988 \pm 0.009$  for both and it was concluded that these positions are essentially fully occupied.

The final  $R$  is 0.070 for 927 structure factors.\* For the 788 structure factors with counting statistics better than two standard deviations  $R=0.044$ . Since these values mainly depend on the agreement of the large  $F$  values of the subcell, they cannot be taken as an indicator for the accuracy of the superstructure. However, the  $R$  of 0.056 for the 329 strongest superstructure  $F$ 's compares favorably with the  $R$  of 0.024 for 244 subcell  $F$ 's of the same intensity range.

### Discussion

The structure of VP<sub>1.75</sub> was refined with 'split' atoms. Since the split-atom positions are too close to each other, only one of any two can be occupied. Thus the near-neighbor environments of all 'equivalent' atoms are slightly different, depending on the actual occupancy of the near split-atom positions. The thermal parameters of V(1), V(2), P(1), and P(2), however, are small and only slightly above those found for similar compounds.† This indicates that their positions are almost independent of the local occupancy of the P(4) and P(5) positions. The latter, together with the fully occupied P(3) positions, are almost coplanar and correspond to the position of the F atom of the PbFCl

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31505 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

† The structures of the high-pressure compounds CrP<sub>4</sub>, CrP<sub>2</sub>, and MnP<sub>4</sub> (Jeitschko & Donohue 1972, 1973, 1975) were all refined from diffractometer data of similar quality as described here for VP<sub>1.75</sub>; in particular they included high-angle data and were corrected for absorption. The  $B$  values varied between 0.21 and 0.27 Å<sup>2</sup> for the metal and between 0.31 and 0.37 Å<sup>2</sup> for the P atoms.

type subcell. The short-range order within that layer can be concluded from an analysis of the P-P distances (Fig. 3.)

Ideal single-bond P-P distances in elemental P modifications and polyphosphides are close to  $2.21 \pm 0.02$  Å (Dahl, 1969; Jeitschko & Donohue, 1975).

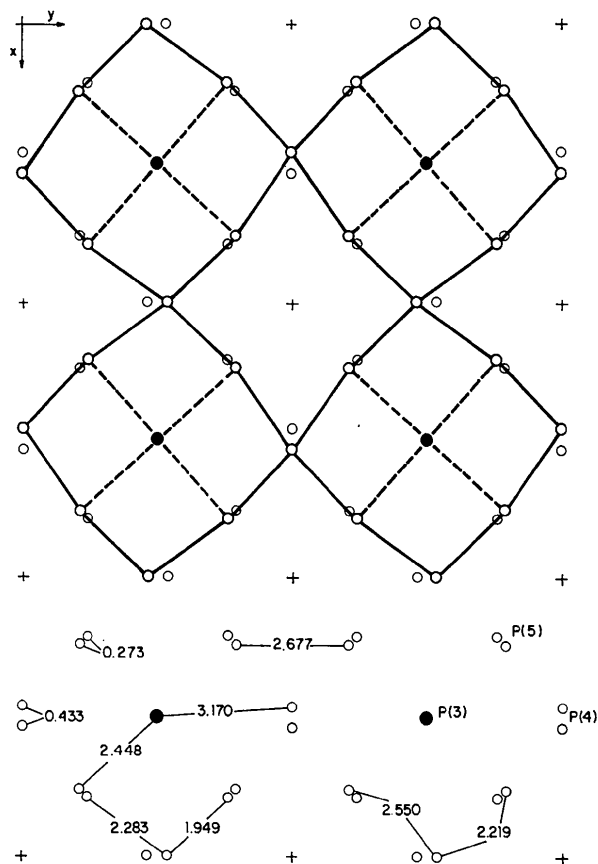


Fig. 3. Phosphorus positions of VP<sub>1.75</sub> corresponding to the fluorine position in the PbFCl type structure. Black dots represent fully occupied P positions. Partially populated P positions are shown with open circles. Crosses indicate the origin of the VP<sub>1.75</sub> cell as given in the abstract, and at the same time they represent vacant F sites of the PbFCl type subcell. In the lower part of the figure P-P distances are indicated in Å. The designations of the P atoms correspond to those of Table 2.

Table 2. Structural parameters of VP<sub>1.75</sub>

Numbers in parentheses are e.s.d.'s in the least significant digits. Thermal parameters ( $\times 10^4$ ) are of the form  $T = \exp(-\sum h_i h_j b_{ij})$ . The last column contains equivalent isotropic  $B$  values.

	$P\bar{4}m2$	Occupancy	$x$	$y$	$z$	$b_{11}$	$b_{22}$	$b_{33}$	$b_{12}$	$b_{13}$	$b_{23}$	$B$ (Å <sup>2</sup> )
V(1)	4( $j$ )	1	0.2502 (1)	0	0.2619 (1)	36 (3)	29 (3)	15 (2)	0	3 (1)	0	0.46 (2)
V(2)	4( $k$ )	1	0.2555 (1)	$\frac{1}{2}$	0.2548 (1)	10 (3)	48 (4)	9 (1)	0	-1 (1)	0	0.38 (2)
P(1)	4( $j$ )	1	0.2480 (2)	0	0.6063 (2)	45 (6)	23 (5)	21 (2)	0	5 (2)	0	0.52 (2)
P(2)	4( $k$ )	1	0.2494 (2)	$\frac{1}{2}$	0.5995 (2)	30 (6)	37 (5)	15 (2)	0	-4 (2)	0	0.46 (2)
P(3)	1( $b$ )	1	$\frac{1}{2}$	$\frac{1}{2}$	0	62 (3)	$b_{11}$	7 (3)	0	0	0	0.71 (4)
P(4)	4( $j$ )	0.367 (5)	0.4658 (4)	0	0.9981 (7)							0.40*
P(5)	8( $l$ )	0.437 (3)	0.2116 (3)	0.2418 (3)	0.0026 (9)							0.40*

\* Held constant, see text.

Larger distances are known and can be ascribed to fractional bonds. However, P-P distances shorter than 2.1 Å are not found in solids. We therefore also assume that both of those P(4) and P(5) positions which are 1.949 Å apart cannot be occupied. This automatically leads to only one model for the short-range order. It is shown in the upper part of Fig. 3 where the positions occupied by P atoms are connected by solid (full) and broken (fractional P-P bonds) lines. If the order proposed by this model were long-range, the translation period would be  $\sqrt{2}$  times bigger than the one given in the abstract (*i.e.*,  $2\sqrt{2}$  times bigger than the  $a$  of the PbFCl type subcell). Since, however, the occupancies of the P(4) and P(5) positions are considerably less than 0.5, frequently neither of the split-atom positions is occupied. This is expected to inhibit long-range order and it is therefore not too surprising that no evidence was found for this 'super'-superstructure even on strongly exposed single-crystal films.

Interatomic distances and near-neighbor coordinations corresponding to this short-range ordered model are listed in Table 3 and shown in Fig. 4. V(1) has eight P neighbors with an average bonding distance of 2.436 or 2.446 Å, depending on the short-range order of the P(4) and P(5) atoms. V(2) has nine P neighbors at the somewhat larger average bond distance of 2.482 Å. P(1) and P(2) are coordinated by five V atoms forming a distorted square pyramid at average bond distances of 2.465 and 2.463 Å respectively. P(3), P(4), and P(5) form P-P bonds as discussed above and in addition each is surrounded by four V atoms which form a distorted tetrahedron. P(4) has four close P neighbors but only three on average, considering partial occupancies.

Although the superstructure of NbP<sub>1.7</sub> was not determined, it appears to be different from the one we found for VP<sub>1.75</sub>. This suggests that possibly a whole series of VP<sub>2-x</sub> and NbP<sub>2-x</sub> phases might exist with

Table 3. *Interatomic distances in VP<sub>1.75</sub>*

Standard deviations are all less than 0.02 Å. All distances shorter than 3.5 Å (for V) and 3.0 Å (for P) are listed. Since P(4) and P(5) were found in split-atom positions, the V(1) atoms obtain two slightly different P(4) and P(5) coordinations. These occur equally often and are listed side by side.

V(1):	2 P(1)	2.426 Å	V(2):	2 P(1)	2.484 Å
	1 P(1)	2.504		2 P(2)	2.454
	2 P(2)	2.449		1 P(2)	2.507
	1 P(4)	2.353 or 2.628		1 P(3)	2.413
	2 P(5)	2.439 or 2.344		1 P(4)	2.458
	1 V(1)	3.160		1 P(5)	2.471
	1 V(1)	3.165		1 P(5)	2.615
	2 V(2)	3.163		2 V(1)	3.163
				1 V(2)	3.093
				1 V(2)	3.232
P(1):	2 V(1)	2.426	P(2):	2 V(1)	2.449
	1 V(1)	2.504		2 V(2)	2.454
	2 V(2)	2.484		1 V(2)	2.507
	2 P(1)	2.703		2 P(1)	2.696
	2 P(2)	2.696		2 P(2)	2.668
P(3):	4 V(2)	2.413	P(5):	1 V(1)	2.344
	4 P(4)	2.448		1 V(1)	2.439
				1 V(2)	2.471
P(4):	1 V(1)	2.353		1 V(2)	2.615
	1 V(1)	2.628		1 P(3)	2.448
	2 V(2)	2.458		1 P(4)	2.219
	2 P(5)	2.219		1 P(4)	2.283
	2 P(5)	2.283		1 P(5)	2.677

various superstructures, all based on a defect PbFCl type subcell, depending on preparation conditions and stoichiometries. Similar ordered defect structures are known for vanadium carbides VC<sub>1-x</sub> based on a NaCl type subcell (see for instance Billingham, Bell & Lewis, 1972; Sauvage & Parthé, 1972), for transition metal chalcogenides T<sub>1-x</sub>X based on a NiAs type subcell [for a summary see Flahaut (1972)] or for defect transition metal disilicides TSi<sub>2-x</sub> with a TiSi<sub>2</sub> type subcell (Jeitschko & Parthé, 1967; Nowotny, 1970). LaTe<sub>1.8</sub>

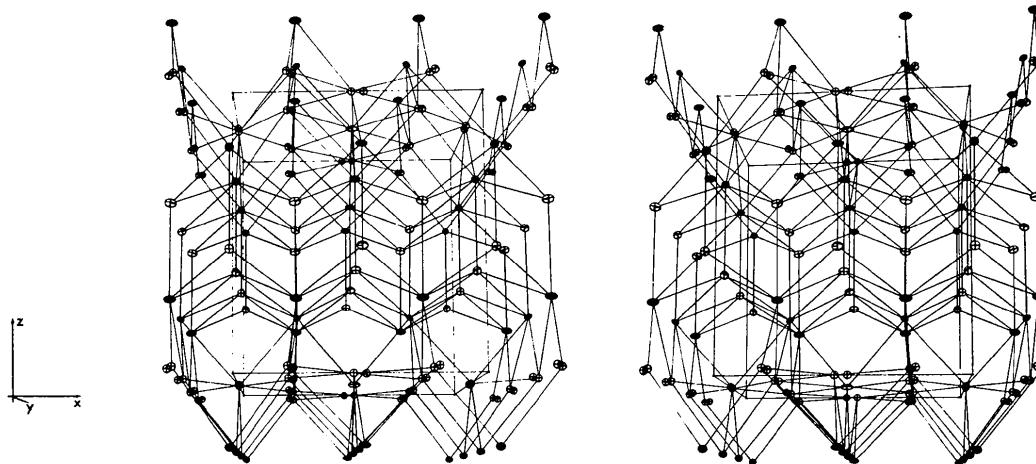


Fig. 4. Stereo drawing of VP<sub>1.75</sub> with ordered defect-PbFCl type structure. V atoms and the P atoms at  $z \sim 0$  are shown as light ellipsoids, P(1) and P(2) atoms are black. Thermal parameters correspond to those of Table 1 at the 50% probability limit. Bonds for the 'split' P atoms correspond to one of the two equivalent short-range order configurations.

has a defect PbFCl type structure similar to the subcell of  $VP_{1.75}$  with defects on the F site of PbFCl; however, no superstructure was observed (Wang, Steinfink & Bradley, 1966). Defect PbFCl type structures were also observed for the *anti*-type ( $Cu_2Sb$  type) compounds  $Cu_{2-x}Te$  (Forman & Peacock, 1949),  $Ni_{2-x}Te$  (Barstad, Grønvold, Røst & Vestersjø, 1966) with  $x \approx 0.5$ , and for compounds of similar compositions (Stevens, 1969). In these compounds, however, the partially occupied sites correspond to the Cl positions of PbFCl.

In Fig. 5 the X-ray densities (determined at normal pressure) of the new high-pressure phases  $VP_{1.75}$  and  $NbP_{1.7}$  are compared with the densities of the ambient-pressure phases in their respective systems. It can be seen that the new phases have only slightly higher densities at ambient pressure, although (being 'defect' structures) they may have higher compressibilities and thus substantially higher densities at high pressure than their competing phases.

It is somewhat surprising that the compounds  $VP_{1.75}$  and  $NbP_{1.7}$  which have vacant sites (and from a geometric viewpoint ideal composition  $TX_2$ ) can successfully compete at high pressure with the ambient-pressure compounds  $VP_2$  and  $NbP_2$ , which have an  $OsGe_2(NbAs_2)$  type structure, a structure with high coordination for all atoms and no defects. From a geometric point of view one could expect that at high pressure the unoccupied sites in the defect PbFCl type compounds  $VP_{1.75}$  and  $NbP_{1.7}$  would be occupied with P atoms to achieve higher density. Obviously directional bonding and nonbonding (lone pairs) characteristics are important in these compounds and prevent close packing.

In PbFCl-type  $NbSiAs$  relative oxidation states were rationalized according to  $Nb^{5+}[Si]^{2-}As^{3-}$  (Johnson & Jeitschko, 1973) where the brackets indicate bonding within the Si layers. These Si atoms correspond to those P atoms of  $VP_{1.75}$  which are shown in Fig. 3. The formal charge (oxidation number) of the P atoms in that layer can be calculated in the usual way by assuming an electron octet for each P atom and subtracting two charges for each full P-P bond (this leads to  $P^{3-}$  for isolated P atoms,  $P^{2-}$  for P-P pairs,  $P^-$  for infinite P chains, etc.). Assuming full P-P bonds for the P-P distances of 2.22 and 2.28 Å and P-P half-bonds for the P-P distances of 2.45 Å, and accounting for the partial occupancies of the P(4) and P(5) sites, one obtains a polyanion with a formal charge of  $-0.67 \pm 0.24$  per P atom\* for a formal oxidation formula  $V^{3.5+}[P_{0.75}]^{10.5-}P^{3-}$ . To obtain a valence formula similar to  $Nb^{5+}[Si]^{2-}As^{3-}$  for  $VP_{1.75}$ , the P-P bonding

in the P layers would need to be reduced. This could be achieved by increasing  $a$  or in part also by reducing the number of P atoms in that layer. Both are opposed by the high pressure. Thus the number of defects in  $V_{1.75}$  can be understood to be a compromise between the strive for normal valence (*i.e.* accommodation of the valence electrons in low energy states) and the requirements of dense packing for a high-pressure compound.

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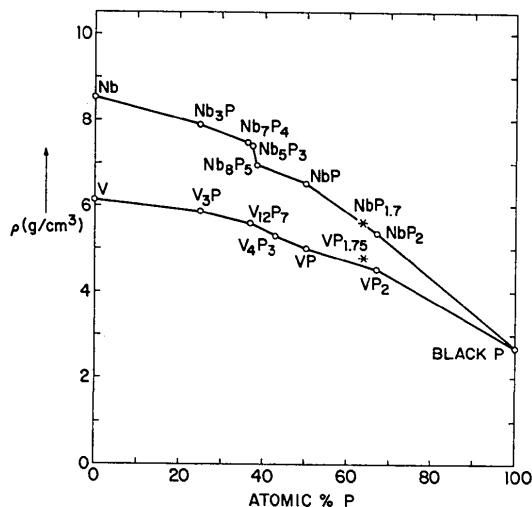


Fig. 5. Densities of the new phases  $VP_{1.75}$  and  $NbP_{1.7}$ , prepared at high pressure, compared to ambient pressure phases in the systems V-P and Nb-P. Data for the ambient pressure phases were taken from Pearson (1967) and recent reports:  $Nb_3P$  and  $NbP_2$  (Rundqvist, 1966a),  $Nb_7P_4$  (Rundqvist, 1966b),  $Nb_5P_3$  (Hassler, 1971),  $Nb_8P_5$  (Anugul, Pontchour & Rundqvist, 1973),  $V_3P$  (Jawad, Lundström & Rundqvist, 1971),  $V_{12}P_7$  (Olofsson & Ganglberger, 1970),  $V_4P_3$  (Boller, 1973),  $VP_2$  (Hulliger, 1964).

\* The error limits in this value result from the uncertainty of whether the voids in the partially occupied sites attract or avoid each other. The calculation is not shown here; however, one can easily convince oneself that the average formal oxidation number of a P atom in that P-polyanion is greater than -1, since the average P atom in that layer has more than two near P neighbors.

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## An Investigation of a Possible C–H···F Interaction in 2-Fluorophenyl Cyanomethyl Sulfone

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Determination of the structure of 2-fluorophenyl cyanomethyl sulfone,  $F(C_6H_4)SO_2CH_2CN$ , was undertaken to investigate a possible C–H···F interaction. Crystals of the compound are orthorhombic, space group *Pbca*;  $a=9.123$  (2),  $b=19.384$  (5),  $c=9.886$  (2) Å,  $V=1748.2$  Å<sup>3</sup>,  $D_x=1.462$  g cm<sup>-3</sup> at  $-40^\circ\text{C}$ ,  $F. W. 199.20$  and  $Z=8$ . Intensities were measured at  $-40^\circ\text{C}$  on a Syntex  $P2_1$  diffractometer with Mo  $K\alpha$  radiation. Full-matrix least-squares refinement of all positional and thermal (anisotropic for non-hydrogen atoms and isotropic for hydrogen atoms) parameters converged at a conventional  $R$  of 0.037 and a weighted  $R$  of 0.039 for 1586 reflections [ $I > 2\sigma(I)$ ]. No C–H···F interaction was observed.

### Introduction

This structure represents the third in a series investigating C–H···N, C–H···O, and C–H···F interactions in compounds in which the C–H bond is polarized by adjacent electron-withdrawing groups. Such an interaction, with a short O···H distance of 2.22 Å, was found in the first compound of the series, 2,4-dinitrobenzyl 4'-tolyl sulfone (Harlow, Pfluger, Sammes & Simonsen, 1974). The study, however, did not establish whether the close contact was due to attractive forces or to other influences. A study of a second compound,

cyanomethyl 2-picoly sulfone, revealed no C–H···O contacts shorter than 2.45 Å (Harlow, Sammes & Simonsen, 1974). It was hoped that the present study of 2-fluorophenyl cyanomethyl sulfone, hereinafter abbreviated FCS, would reveal a geometry which would not force, but would allow close contact between methylene hydrogen atoms and the fluorine atom and would yield additional information about the nature of this type of interaction. A sample of FCS was generously supplied to the authors by Dr M. P. Sammes, who synthesized all three compounds of this series.