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A neutron diffraction investigation of V_8C_7.

By A. W. HENFREY* and B. E. F. FENDER, *Inorganic Chemistry Laboratory, University of Oxford, Oxford, England.*

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V_8C_7 has been examined by neutron diffraction. The occupation numbers obtained are very close to those expected for a perfect spiral array of vacancies on the carbon sub-lattice. There is no indication of a displacement of carbon atoms.

The main structural feature of the grossly non-stoichiometric Group IVA and VA quasi-metallic compounds is the extensive composition range of the NaCl phase. However, recently a number of ordered superstructure phases have been reported including TiO (Watanabe, Castles, Jostsons & Malin, 1967), TiO (Goretzki, 1967), Ti_2N (Lobier & Marcon, 1969), Th_4C_3 (Lorenzelli, 1969), V_6C_5 (Lye, Venables & Kahn, 1968), V_8C_7 (De Novion, Lorenzelli & Costa, 1966; Kordis, 1968; Alyamovskii, Ge'ld, Shveikin & Schetnikov, 1968). The latter two compounds both exhibit a spiral array vacancies and this type of structural arrangement also occurs in other quasimetallic compounds [*e.g.* titanium silicides (Nowotny, 1970)].

The V_8C_7 compound belongs to the $P4_132$ space group (or its enantiomorph) as first demonstrated by De Novion, Lorenzelli & Costa (1966) and this structure is also in accord with the ^{51}V nuclear magnetic resonance results of Froidevaux & Rossier (1968). The possibility that spiral structures will emerge as the basis of a range of ordered quasi-metallic compounds warrants detailed investigation and in the course of a study of non-stoichiometric niobium and vanadium carbides we have determined the neutron-diffraction powder pattern of V_8C_7. Because the vanadium scattering length is very small ($b_V = -0\cdot05 \times 10^{-12}$ cm) only scattering from the carbon atoms contributes effectively to the Bragg intensities. The neutron method is therefore particularly valuable in assessing the completeness of the ordered vacancy–carbon array as well as providing an indication of how closely the carbon atoms are located on special positions.

Samples near the theoretical composition of V_8C_7 were prepared by heating pelleted mixtures of vanadium metal (supplied spectrographically standardized by Johnson Matthey Chemicals Ltd.) and graphite powder (supplied with an impurity level lower than 10 p.p.m. by Koch Light Laboratories) for a total of 100 hours at 1650°C. Analysis for vanadium was carried out by quantitative conversion to V_2O_5 and the total carbon content was determined as $BaCO_3$. The free carbon content was less than 0·03% by weight and the oxygen content was determined by vacuum fusion to be in the range 0·02 to 0·06 weight %. Two samples of composition $VC_{0\cdot865}$ and $VC_{0\cdot863}$ were prepared.

X-ray powder photographs showed all the low angle lines (up to $2\theta \simeq 65°$) for the $P4_132$ space group except the 311 peak. The calculated lattice parameters were $8\cdot3307 \pm 0\cdot0009$ ($VC_{0\cdot865}$) and $8\cdot3303 \pm 0\cdot0007$ ($VC_{0\cdot863}$); values which are slightly lower than those previously reported by Kordis (1963) (8·3334 for $VC_{0\cdot88}$) and De Novion *et al.* (1966) (8·3340 for $VC_{0\cdot89}$). The smaller parameters probably arise from a lower oxygen content on the present samples. It is known that oxygen increases the apparent lattice parameter (Storms, 1967; Storms & Krikorian, 1960) and it has been suggested that the De Novion sample contained 1–2% oxygen (Froidevaux & Rossier, 1968).

Neutron Bragg intensities were measured up to $2\theta \simeq 55°$, using neutrons with a wavelength of 1·053 Å. The intensity of peaks beyond 400 (except the 421 and 440) could not be measured accurately because the peaks overlapped extensively, but peak intensities up to and including the 400, plus the 421 and 440 peaks, were refined to give a best least-squares fit in terms of a scale factor, a temperature factor for carbon and three carbon occupation numbers. Table 1 shows there is good agreement between calculated and observed structure factors for $VC_{0\cdot863}$ at 4·2°K in terms of parameters based on the $P4_132$ space group. Similar agreement is obtained with room temperature measurements on this sample and on $VC_{0\cdot865}$ (Table 2).

Table 1. *Experimental and calculated structure factors for* $VC_{0\cdot863}$ *at* 4·2°K

hkl	F_{obs}*	F_{calc}
110	1·01±0·05	1·11
111	1·40±0·08	1·34
210	2·08±0·07	2·15
211	1·18±0·06	1·11
310	1·58±0·14†	1·11
311	1·33±0·07†	1·34
222	19·80±0·04	20·02
320	2·54±0·09†	2·14
321	1·43±0·09†	1·11
400	17·26±0·07	16·81
421	1·97±0·14	2·14
440	16·73±0·03	16·72

* Error given is standard error arising from counting statistics.

† Actual error is considerably larger because peaks overlap.

Not only do the neutron diffraction results confirm the space group derived from X-ray studies but it is seen that the occupation numbers agree well with the expected values, assuming a perfect spiral array. Taking the average of the of the three determinations there is however some indication of a slight excess of C′ carbon atoms at the expense of a deficiency of C″ atoms. The low values of the apparent temperature factor indicate that the carbon atoms are closely located on special positions and this was confirmed by a worsening of the *R* value on displacing atoms from these positions.

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* S.R.C. Research Student

Table 2. *Structure parameters of average cell*

	Coordinates of $P4_132$ space group			Occupation number (experimental)*			Occupation number (ideal)†
	x	y	z	$VC_{0.863}$ (4·2°K)	$VC_{0.863}$ (300°K)	$VC_{0.865}$ (300°K)	
V	$\frac{3}{8}$	$\frac{3}{8}$	$\frac{3}{8}$				0·333
V	$\frac{1}{8}$	$\frac{3}{8}$	$\frac{1}{8}$				1·000
C′	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	0·186 ± 0·008	0·181 ± 0·017	0·183 ± 0·007	0·165
C″	$\frac{1}{8}$	$\frac{5}{8}$	$\frac{5}{8}$	0·480 ± 0·010	0·472 ± 0·024	0·478 ± 0·010	0·493
C″	$\frac{1}{8}$	$\frac{3}{8}$	$\frac{7}{8}$	0·497 ± 0·009	0·503 ± 0·023	0·475 ± 0·009	0·493
Temperature factor (carbon)				0·1 Å^2	0·2 Å^2	0·2 Å^2	
Reliability (R) value				3·4%	5·8%	3·4%	

* Refinements based on a carbon scattering length of $0{\cdot}663 \times 10^{-12}$ cm.

† Calculated assuming small vacancy excess on ideal V_8C_7 composition is randomly distributed.

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A note on the crystal structure of α-CdP_2.

By Olle Olofsson and Jan Gullman, *Institute of Chemistry, University of Uppsala, S-751 21 Uppsala, Sweden*

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The single-crystal data recorded by Goodyear & Steigmann for α-CdP_2 have been further refined. The resulting distances are in better agreement with distances in other known phosphides of similar type.

Recently, Goodyear & Steigmann (1969) described the determination of the crystal structure of α-CdP_2. One characteristic feature of the structure is chains of phosphorus atoms running parallel to each other in the **c** direction. There are two different P–P distances within the chains. According to Goodyear & Steigmann these distances are 2·05 and 2·39 Å respectively. It seemed to us that these distances deviated considerably from what was to be expected from a consideration of other known polyphosphides with similar arrangements of phosphorus atoms. In particular, the 2·05 Å distance is very short in comparison with the normal P–P bond distance of 2·20 Å.

Despite the fact that Goodyear & Steigmann claim that the least-squares refinement was stopped when the last shifts were less than the standard deviations, we decided to try to see if it was possible to make a further refinement using their observed structure factors. We used a local version of the least-squares program *LALS* originally written by P. K. Gantzel, R. A. Sparks and K. N. Trueblood, Los Angeles, U.S.A.

Table 1. *Atomic parameters with standard deviations*

For each atom the result from the present refinement is given in the first row, and the result of Goodyear & Steigmann in the second row.

	x	y	z	B
Cd	0·1529 (2)	0·1011 (3)	0·2606*	1·89 (8) Å^2
	0·1529 (3)	0·1016 (5)	0·2606 (26)	1·95 (5)
P(1)	0·1185 (7)	0·4442 (14)	0·5957 (23)	1·43 (12)
	0·1186 (10)	0·4458 (21)	0·5850 (30)	1·34 (16)
P(2)	−0·0064 (7)	0·2693 (12)	−0·1036 (24)	1·24 (12)
	−0·0074 (10)	0·2697 (19)	−0·0676 (33)	1·16 (15)

* Arbitrary.