MEAGHER, E. P., TOSSELL, J. A. & GIBBS G. V. (1978). *Phys. Chem. Miner.* In the press.
O'KEEFFE, M. & HYDE, B. G. (1976). *Acta Cryst.* B**32**, 2923–2936.
O'KEEFFE, M. & HYDE, B. G. (1978). *Acta Cryst.* B**34**, 27–32.
TAYLOR, D. (1972). *Mineral. Mag.* **38**, 629–631.
TOSSELL, J. A. & GIBBS, G. V. (1977). *Phys. Chem. Miner.* **2**, 21–57.
TOSSELL, J. A. & GIBBS, G. V. (1978). *Acta Cryst.* A**34**, 463–472.

Acta Cryst. (1979). B**35**, 30–33

Redetermination of the Crystal Structure of $Cr_{12}P_7$

BY HEI KYUNG CHUN* AND G. B. CARPENTER

Department of Chemistry, Brown University, Providence, RI 02912, *USA*

(*Received* 27 *June* 1978; *accepted* 12 *September* 1978)

Abstract

Crystals of $Cr_{12}P_7$ are hexagonal, space group $P6_3/m$, with $a = 8{\cdot}981$ (2) and $c = 3{\cdot}313$ (2) Å. The material is isotypic with Th_7S_{12}. All atoms lie on mirror planes. Chromium atoms are coordinated by either five phosphorus atoms in a distorted square pyramidal arrangement, or by four in a distorted tetrahedral arrangement. One phosphorus atom is disordered between two positions, and half of the chromium atoms exhibit disorder coupled to that of the phosphorus atoms. The average Cr—P distance in the part of the structure least affected by disorder is 2·392 Å. Extra reflections in the *hk*0 layer require a sevenfold larger superlattice with $\mathbf{A} = 2\mathbf{a} - \mathbf{b}$, $\mathbf{B} = \mathbf{a} + 3\mathbf{b}$, $\mathbf{C} = \mathbf{c}$.

Introduction

Several workers have reported structural data for the chromium phosphide of stoichiometry $Cr_{1.7}P$, but certain features have remained ambiguous. Lundström (Aronsson, Lundström & Rundqvist, 1965) indexed the diffraction pattern from powder samples on a hexagonal cell, and reported $a = 15{\cdot}552$, $c = 3{\cdot}319$ Å for a chromium-rich preparation, $a = 15{\cdot}536$, $c = 3{\cdot}313$ Å for a phosphorus-rich preparation. Later Lundström (1969) suggested that the compound has the anti-Th_7S_{12} structure (Zachariasen, 1949); this description presumably implies a smaller cell with $a = 15{\cdot}55/\sqrt{3} = 8{\cdot}98$ Å, space group $P6_3/m$, and disorder at least among some phosphorus atoms – all in analogy with Th_7S_{12}. Baurecht, Boller & Nowotny (1971) carried out a single-crystal photographic study leading to $a = 8{\cdot}977$, $c = 3{\cdot}316$ Å and a structure in space group $P\bar{6}$ that is essentially the anti-Th_7S_{12} type except that no disorder is present.

The availability of good single crystals prompted us to attempt to clarify the details and improve the accuracy of the structure by use of diffractometer data. In the course of this study the existence of a superlattice became evident.

Experimental

Shiny dark-brown plate-like crystals of composition $Cr_{1.7}P$ were grown by chemical vapor transport by Dr R. Madar in the laboratory of Professor A. Wold. Dr Madar also measured the density of the crystals by the method of Archimedes.

Preliminary photographic study confirmed the cell dimensions reported by Baurecht *et al.* (1971). However, systematic absences were noted for reflections 00*l* with *l* odd, reflections that they had not examined. The Laue symmetry was evidently 6/*m*, so the possible space groups are $P6_3/m$ and $P6_3$; the former was shown to be correct by the structure determination. Furthermore, photographs showed a few weak superlattice reflections, all with $l = 0$ and conforming to 6/*m* symmetry. Baurecht *et al.* (1971) had looked for superlattice reflections [in an attempt to explain Lundström's original cell (Aronsson *et al.*, 1965)], but failed to find any from their crystals.

A crystal of approximate dimensions 0·04 × 0·13 × 0·44 mm was cut from a larger plate, mounted along *c* (the long axis of the specimen), and selected for intensity measurements on the basis of freedom from twinning and reasonably narrow mosaic spread (0·14°). Twelve reflections, scattered through reciprocal space, were carefully centered, and their angle settings were used to refine the cell dimensions by least-squares fitting. The crystal data are summarized below.

---

* Present address: Department of Chemistry, Cornell University, Ithaca, NY 14853, USA.

0567-7408/79/010030-04$01.00

Crystallographic data

Hexagonal, Laue symmetry $6/m$, systematic absences: $00l$ with $l = 2n + 1$, $d_m = 6{\cdot}0$–$6{\cdot}4$, $d_x = 6{\cdot}03$ Mg m^{-3}. Average cell: contents $Cr_{12}P_7$, $a = 8{\cdot}981$ (2), $c = 3{\cdot}313$ (2) Å, space group $P6_3/m$. Supercell: contents $7 \times Cr_{12}P_7$, $A = 23{\cdot}761$ (5), $C = 3{\cdot}313$ (2) Å, $\mathbf{A} = 2\mathbf{a} - \mathbf{b}$, $\mathbf{B} = \mathbf{a} + 3\mathbf{b}$, $\mathbf{C} = \mathbf{c}$.

Intensity data were collected by means of a computer-controlled Picker FACS-1 diffractometer with Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å) selected by a graphite monochromator; θ–2θ scans were used. The scan range was 1·4° in 2θ, at a rate of 1° min^{-1}; 10 s background counts were made at each end of the scan. Three standard reflections were monitored after every 100 reflections; no systematic drift was found. A total of 568 reflections were measured in the 2θ range from 5 to 52°.

Structure factors were extracted in the usual way, and standard deviations were estimated by taking into account statistical errors in counting, round-off errors in the FACS-1 system, and so-called instabilities. The variance in F^2 was thus expressed in the form

$$\sigma(F^2)^2 = (1/L_P)^2\,[C + (t_c/2t_b)^2\,(B_1 + B_2) + 434 + (0{\cdot}01C)^2]$$

where L_P is the Lorentz–polarization factor, C is the total count measured in time t_c, and B_1 and B_2 are background counts each measured in time t_b. The corresponding estimated standard deviation for a structure factor magnitude was approximated by the expression

$$\sigma(F) = \sigma(F^2)/2F.$$

In view of the linear absorption coefficient of 15·1 mm^{-1}, absorption corrections were applied by a modified version of Hamilton's *GONO* 9 program, the logic of which has been outlined (Hamilton, 1957). Transmission factors ranged from 0·20 to 0·45. The corrected structure factors for equivalent reflections were then averaged to yield 179 independent structure factors, including 'unobserved' reflections.*

Subsequently, diffractometer measurements were made of those superlattice reflections that could be seen on photographs. The relative structure factor magnitudes, on approximately the same scale as the main reflections, have been deposited.*

Structure determination and refinement

Only the average structure is discussed in this section and the next; the supercell is described subsequently. Analysis of the Patterson function confirmed that the structure is the anti-Th_7S_{12} type. The large peaks were all in the planes $w = 0$ and $\frac{1}{2}$, thereby indicating occupancy of special positions in $P6_3/m$ rather than general positions in $P6_3$. Least-squares refinement was carried out by means of the program *BULS*, a local modification of *ORFLS* (Busing, Martin & Levy, 1962); the quantity $\sum w(F_o - F_c)^2$ was minimized with weights taken as $w = 1/\sigma(F)^2$. All reflections were used. Atomic scattering factors for neutral atoms were taken from Cromer & Waber (1965) and corrections for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1962).

Initial stages of refinement proceeded with two chromium atoms and one phosphorus atom in positions $6(h)m$ $(x,y,\frac{1}{4};\ldots)$ and with two half-atoms of phosphorus in positions $2(a)\bar{6}$ $(0,0,\frac{1}{4};\ 0,0,\frac{3}{4})$. With anisotropic temperature factors this structure refined to $R_w = 0{\cdot}066$ (with 002 and 004 omitted, reflections that appeared to be appreciably in error because of extinction or imperfectly corrected absorption). One of the two independent chromium atoms was so markedly elongated that it was necessary to consider the possibility of disorder for this atom as well as for one kind of phosphorus atom. A difference map showed that the offending chromium atom is split into two half-atoms. When refinement was continued with two half-atoms, they moved to positions 0·48 Å apart, and the discrepancy indices fell to $R = 0{\cdot}058$, $R_w = 0{\cdot}044$. In the final cycle of refinement, all shifts were less than one-fourth of their estimated standard deviations. In this refinement the thermal motions for all atoms, which lie on mirror planes, were constrained to obey $\beta_{13} = \beta_{23} = 0$; the disordered phosphorus and chromium atoms were required to be cylindrically symmetric ($\beta_{11} = \beta_{22} = 2\beta_{12}$). For phosphorus this constraint is required by the $\bar{6}$ point symmetry; for chromium it is the simplest way to separate the highly correlated position and thermal motion of neighboring half-atoms. The final positional parameters* are given in Table 1. A final difference map was essentially featureless; the largest

Table 1. *Final parameters for* $Cr_{12}P_7$

All parameters and their standard deviations (in parentheses) have been multiplied by 10^4.

	x	y	z
Cr(1)	5109 (1)	3740 (1)	2500
Cr(2)*	2108 (5)	144 (4)	2500
Cr(3)*	2638 (4)	137 (3)	2500
P(1)*	0	0	2500
P(2)	2851 (2)	4462 (3)	2500

* Occupancy factor 0·5.

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33946 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* See previous footnote.

peak had electron density 0·76 e Å^{-3}, at (0·30, −0·46, 0·24) and equivalent positions. The x and y coordinates for chromium and phosphorus atoms are similar to those of Baurecht *et al.* (1971), after interchanging x and y; the root-mean-square difference in fractional coordinates is 0·017 and the maximum difference is 0·047 (for a disordered chromium atom).

It is apparent from the thermal parameters that the motions of atoms Cr(3) and P(2) are highly anisotropic in the final structure. This fact may well indicate that further minor positional disorder is present; unfortunately the limited number of independent reflections would not support the introduction of the additional parameters that would be needed to describe such disorder.

Description and discussion of the structure

An *ORTEP* drawing (Johnson, 1965) of the crystal structure in projection is shown in Fig. 1, and some important interatomic distances are set out in Table 2. All atoms lie on mirror planes at $z=\frac{1}{4}$ and $\frac{3}{4}$. The structure is isostructural with Th_7S_{12} (Zachariasen, 1949), as was suggested by Lundström (1969), and is very similar to that reported by Baurecht *et al.* (1971).

Phosphide structures can be readily and usefully described in terms of polyhedra formed by phosphorus atoms, as has been pointed out by Fruchart and coworkers (Roger, Sénateur & Fruchart, 1969). In $Cr_{12}P_7$ phosphorus atoms divide the crystal into small polyhedra of three kinds, approximately described as square pyramids, tetrahedra, and trigonal prisms. Pyramids and tetrahedra alternate along columns extending in the **c** direction, as shown in Fig. 2. Prisms are stacked one above another to form another kind of column. These different kinds of columns all project into triangles in Fig. 1. There are 26 polyhedra in one unit cell: 18 pyramids, 6 tetrahedra, and 2 prisms. Half of the pyramids and tetrahedra are occupied by the 12 chromium atoms, whereas all prisms are empty.

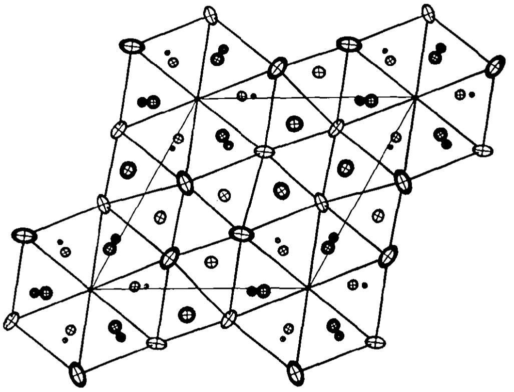


Fig. 1. Projection of the average structure of $Cr_{12}P_7$ on the (001) plane. The heavily outlined atoms lie at $z=\frac{3}{4}$, the lightly outlined ones at $z=\frac{1}{4}$. The lines connect phosphorus atoms.

The vacant polyhedra of phosphorus atoms are not too small to contain chromium atoms; rather, the presence of chromium atoms in adjacent sites excludes atoms from the empty sites. The center of a trigonal prism is surrounded by three chromium atoms, each only 1·614 Å away, in adjacent pyramids. The center of each empty pyramid or tetrahedron is surrounded by chromium atoms above and below at a distance of $c/2$ = 1·656 Å and by others at the same height less than 1·5 Å distant. On the other hand, the sites that are occupied by chromium atoms have no neighboring chromium atoms closer than 2·625 Å.

Table 2. *Interatomic distances* (Å) *in* $Cr_{12}P_7$

The estimated standard deviations are all in the range 0·001 to 0·002 Å. The transformations implied by the superscripts are the following:

(i)	$1-x$,	$1-y$,	$\frac{3}{4}$
(ii)	$1-x$,	$1-y$,	$-\frac{1}{4}$
(iii)	y,	$y-x$,	$\frac{3}{4}$
(iv)	y,	$y-x$,	$-\frac{1}{4}$
(v)	$x-y$,	x,	$\frac{3}{4}$
(vi)	$-x$,	$-y$,	$\frac{3}{4}$
(vii)	x,	y,	$\frac{5}{4}$

Pyramid containing Cr(1)

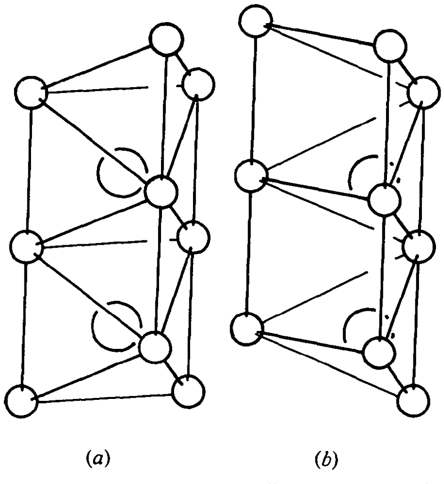
Cr(1)–P(2)		2·418
Cr(1)–P(2^{i})	(×2)	2·398
Cr(1)–P(2^{iii})	(×2)	2·372
P(2)–P(2^{i})	(×2)	3·853
P(2)–P(2^{iii})	(×2)	3·886
P(2^{i})–P(2^{ii})	(×2)	3·313
P(2^{i})–P(2^{iii})	(×2)	3·123

Pyramid containing Cr(2)

Cr(2^{v})–P(2)	(×2)	2·483
Cr(2^{v})–P(2^{iii})		2·497
Cr(2^{v})–P(1)	(×2)	2·470
P(1)–P(1^{vii})	(×2)	3·313
P(1)–P(2)	(×2)	3·515
P(1)–P(2^{iii})	(×2)	3·886
P(2)–P(2^{iii})	(×2)	3·886

Tetrahedron containing Cr(3)

Cr(3^{v})–P(2)	(×2)	2·239
Cr(3^{v})–P(2^{iii})		2·362
Cr(3^{v})–P(1^{vi})		2·310
P(1^{vi})–P(2)	(×2)	3·886
P(1^{vi})–P(2^{iii})		3·515
P(2)–P(2^{iii})	(×2)	3·886
P(2)–P(2^{vii})		3·313



(*a*) (*b*)

Fig. 2. Disorder in $Cr_{12}P_7$. The smaller circles are phosphorus atoms, the larger, chromium atoms. The **c** direction is vertical. In (*a*) the phosphorus atoms P(1) on the left of the column are at heights $z=\frac{1}{4}$ *etc.*, and the chromium atoms occupy square pyramids. In (*b*) the phosphorus atoms on the left are at heights $z=\frac{3}{4}$ *etc.*, and the chromium atoms occupy tetrahedra. The crystallographically determined structure is the average of local structures (*a*) and (*b*).

The disorder appearing as two half-atoms of phosphorus, P(1), is coupled to the disorder appearing as two half-atoms of chromium, Cr(2) and Cr(3), as shown in Fig. 2. The phosphorus atoms P(1) on the left of each column are disordered: in (*a*) they are located at $z = \frac{1}{4}$ *etc.*, and in (*b*) at $z = \frac{3}{4}$ *etc.* In any one small region of the crystal the local ordering is that shown in either (*a*) or (*b*). In (*a*) the chromium atoms [Cr(2)] are near the centers of square pyramids, whereas in (*b*) the chromium atoms [Cr(3)] find themselves in tetrahedra, and they adjust their positions by moving to the right, by about 0·5 Å relative to their positions in (*a*), so as to be near the centers of the tetrahedra. There are six such columns around the phosphorus atoms P(1) at the origin in Fig. 1; the occupied polyhedra are alternately pyramids or tetrahedra around the **c** axis. The pyramids and tetrahedra are interchanged for the two choices of phosphorus position, $0,0,\frac{1}{4}$ and $0,0,\frac{3}{4}$.

The disorder just described can hardly be confined entirely to P(1), Cr(2), and Cr(3). The other atoms P(2) and Cr(1) must shift slightly from their average positions, in response to their local environment. This further disorder is suggested also by the aspherical thermal motion of atom P(2). The limited extent of the data do not justify the introduction of additional parameters to analyze the disorder in greater detail.

The complicated bonding pattern in $Cr_{12}P_7$ is dominated by Cr–P interactions, but Cr···Cr and P···P interactions may also be significant. The five Cr–P distances within one distorted square pyramid are similar, although the apical distance is the longest. The average Cr–P distance is 2·392 Å about Cr(1), 2·480 Å about Cr(2); the latter, and two of its five phosphorus neighbors, are markedly disordered. The four Cr(3)–P distances in a distorted tetrahedron span a range of 0·12 Å with an average of 2·287 Å; Cr(3) and one of its phosphorus neighbors are markedly disordered. All shortest Cr···Cr distances are somewhat longer; the minimum is 2·63 Å between Cr(1) and Cr(3). The P···P distances are longer still; the minimum is 3·12 Å between $P(2^{i})$ and $P(2^{ii})$. In view of the extensive disorder in this structure, a more detailed discussion is omitted.

The superlattice in $Cr_{12}P_7$

Additional weak reflections were observed in Weissenberg and precession photographs of the layer $l = 0$, and were subsequently measured by diffractometer. These reflections were in three clusters, around 220, 270, and 630 (and regions equivalent by the sixfold symmetry). The clusters were densely enough populated with observable reflections so that indexing them on a commensurable superlattice was easy. The reciprocal lattice of the supercell is related to that of the small cell by the transformation

$$\mathbf{A}^* = \tfrac{1}{7}\mathbf{a}^* + \tfrac{2}{7}\mathbf{b}^*, \quad \mathbf{B}^* = -\tfrac{2}{7}\mathbf{a}^* + \tfrac{3}{7}\mathbf{b}^*, \quad \mathbf{C}^* = \mathbf{c}^*$$

and the corresponding direct-cell transformation is given under *Crystallographic data.* The symmetry is the same for both cells. The lengths of the axes are related by $A = \sqrt{7}a$ and the volume of the supercell is seven times that of the small cell.

The existence of the superlattice implies that, superimposed on the disorder described for the average cell, there is a longer-range order that yields a sevenfold larger ordered (or at least partially ordered) cell. Many attempts were made to find a model that might explain how the disordering is coupled among seven small cells so as to achieve this, in spite of the difficulty of inventing a physically reasonable mechanism. A difference Patterson map, also, was calculated from superlattice reflections only. No model consistent with the data could be found.

We gratefully acknowledge support for part of this work from the Materials Research Laboratory at Brown University, funded by the National Science Foundation. We thank Dr Madar and Professor Wold for the gifts of the crystals and the suggestion of the problem.

References

ARONSSON, B., LUNDSTRÖM, T. & RUNDQVIST, S. (1965). *Borides, Silicides and Phosphides*, p. 26. London: Methuen.

BAURECHT, H. E., BOLLER, H. & NOWOTNY, H. (1971). *Monatsh. Chem.* **102**, 373–384.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.

HAMILTON, W. C. (1957). *Acta Cryst.* **10**, 629–634.

International Tables for X-ray Crystallography (1962). Vol. III, p. 215. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

LUNDSTRÖM, T. (1969). *Ark. Kemi*, **31**, 227–266.

ROGER, A., SÉNATEUR, J.-P. & FRUCHART, R. (1969). *Ann. Chim.* (*Paris*), **4**, 79–91.

ZACHARIASEN, W. H. (1949). *Acta Cryst.* **2**, 288–291.