

High-Pressure CrP₂ and CrAs₂ with OsGe₂-Type Structure and Crystal Chemistry of Transition-Metal Dipnictides

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(Received 16 October 1972; accepted 11 December 1972)

The title compounds were prepared from elemental components by reaction at pressures of 65 kbar and temperatures between 1000 and 1200°C. CrP₂ is a metallic conductor and Pauli-paramagnetic. Its crystal structure was determined from single-crystal X-ray counter data and refined to a conventional *R* value of 3% for 253 observed reflections. It is of the OsGe₂ type with lattice constants $a=8.213$ (2), $b=3.034$ (1), $c=7.098$ (2) Å, $\beta=119.47$ (2)°, space group *C2/m*, *Z*=4. CrAs₂ was found from X-ray powder data to have the same structure: $a=8.893$ (1), $b=3.273$ (1), $c=7.389$ (1), $\beta=119.88$ (1). The structure of CrP₂ and its relation to other transition-metal dipnictides are discussed. Two families of transition-metal dipnictides can be distinguished. One has structural characteristics of semiconductors with low near-neighbor coordinations. It is represented by compounds with the marcasite, pyrite, arsenopyrite, and related structures, which occur with transition metals of the iron and platinum metal groups. The other family of transition-metal dipnictides with OsGe₂, PbCl₂, MoP₂, TiAs₂, and CuAl₂-type structures is distinguished by its tendency to have higher coordination numbers, which are characteristic of metallic structures. They are found for transition metals of the titanium, vanadium, and chromium group. The applicability of the generalized (8-*N*) rule for these structures is discussed.

Introduction

During a high-pressure study of the chromium-phosphorus system the phase CrP₄ was found and characterized (Jeitschko & Donohue, 1972). The present paper deals with CrP₂, the only other high-pressure phase found in the phosphorus-rich section of that system. An ambient pressure phase with that composition has been reported previously (Faller, Biltz, Meisel & Zumbusch, 1941). The Debye-Scherrer pattern given in that publication for CrP₂ does not resemble the powder diagram of our high pressure CrP₂. Similarly CrAs₂ reported here is most likely a genuine high-pressure phase since previous investigations of the chromium-arsenic system at low pressures did not give indications of a phase between CrAs and As (Boller, Wolfgruber & Nowotny, 1967; Baurecht, Boller & Nowotny, 1970 and 1971). At ambient pressures Holseth & Kjekshus (1968) have tried to prepare CrP₂ and CrAs₂ under a variety of different thermal conditions without success.

Sample preparation and properties

Samples were prepared from high-purity (>99.9%) elemental components, ground together in transition metal: metalloid ratios varying between 1:2 and 1:2.5. They were cold-pressed and placed in a boron nitride crucible surrounded by a graphite-sleeve heater which was inserted in a pyrophyllite tetrahedron. High pressure was applied with a tetrahedral anvil press of National Bureau of Standards design (Lloyd, Hutton &

Johnson, 1959). Temperature was measured with a Pt-Pt/Rh thermocouple, uncorrected for pressure effects, which was placed at the surface of the cylindrical graphite-sleeve heater. Detailed operating procedures have been described by Bither, Gillson & Young (1966).

CrP₂

Optimum conditions for the preparation of CrP₂ are 1200°C and 65° kbar. After 2 h the samples were slow cooled to 1000°C over 2 hours and then quenched. Because of the large temperature gradient, outer sections of the sample consisted of CrP which was identified through its X-ray powder pattern. It is of MnP type structure, which is also found for CrP at normal pressure (Nowotny & Henglein, 1938). The center section of the sample was mainly CrP₂. Single-phase material was readily distinguishable through its uniform appearance. Chemical analysis gave 44.2 wt. % Cr and 55.5 % P as compared with 45.6 % Cr and 54.4 % P calculated for CrP₂.

X-ray powder photographs were recorded with a Hägg-Guinier camera (Cu *K*α) and evaluated with a David-Mann film reader. High-purity KCl ($a=6.2931$ Å) was used for internal calibration. The patterns were indexed with the unit cell found from single crystals. A least-squares refinement resulted in the lattice constants listed in Table 1. Variations in lattice constants of up to ±0.01 Å were found for different preparations. Thus standard deviations given in Table 1 do not reflect variations in composition. The pycnometric density determined by displacement in bromoform was 4.90 g cm⁻³ as compared with 4.92 g cm⁻³ calculated assuming four formula units.

* Contribution No. 1981.

Table 1. *Lattice constants of the high-pressure phases CrP₂ and CrAs₂*

| | CrP ₂ | CrAs ₂ |
|----------------------------|------------------|-------------------|
| <i>a</i> (Å) | 8.213 (2) | 8.893 (1) |
| <i>b</i> (Å) | 3.034 (1) | 3.273 (1) |
| <i>c</i> (Å) | 7.098 (2) | 7.389 (1) |
| β (°) | 119.47 (2) | 119.88 (1) |
| <i>V</i> (Å ³) | 153.93 (6) | 186.50 (3) |

Crystals of CrP₂ were black and brittle with shiny glass-like fracture surfaces. Electric resistivity measurements with the four-probe technique on a single crystal of unknown orientation showed good metallic conductivity: $\rho(4.2^\circ\text{K}) = 2 \times 10^{-7}$ ohm cm, $\rho(298\text{K}) = 3 \times 10^{-5}$ ohm cm. Magnetic measurements between 4.2 and 298°K showed no detectable magnetic moment indicating diamagnetic or (considering the metallic conductivity) Pauli-paramagnetic behavior. The method employed is not sensitive enough to distinguish between the two.

Attempts to prepare CrP₂ at lower pressures (30–45 kbar) under similar thermal conditions gave multiple-phase products. Their X-ray patterns showed CrP and CrP₄ but not CrP₂. One attempt was also made to prepare the 'normal-pressure' CrP₂ phase reported by Fallner, Biltz, Meisel & Zumbusch (1941). A powder mixture of Cr + 2P was sealed in a silica tube and held at 600°C for two weeks. After that treatment the reaction product contained large amounts of white phosphorus. Another anneal at 500°C for one week gave the same result.

CrAs₂

Reaction temperatures for CrAs₂ varied between 800 and 1200°C. Again a slight excess of As, corresponding to the overall composition CrAs_{2.2}, was used. After two hours at 65 kbar the samples were quenched under pressure. Because of the temperature gradient the material was again multiple phase with a Cr-rich phase at the flat faces of the cylinder and an As-rich phase in the center section. The different regions of the sample were again readily distinguished by their different colors which varied between grey and black. CrAs₂ crystals were identified through their X-ray powder pattern which is very similar to that of CrP₂. An intensity calculation for CrAs₂ (Yvon, Jeitschko & Parthé, 1969) using positional parameters as found for CrP₂ gave very good agreement between observed and calculated intensities (Table 2). Refined lattice parameters for CrAs₂ are listed in Table 1. CrAs₂ is a metallic conductor: $\rho(4.2^\circ\text{K}) = 3 \times 10^{-4}$ ohm cm, $\rho(298^\circ\text{K}) = 5 \times 10^{-3}$ ohm cm.

Structure of CrP₂

Unit cell and space group

Single crystals of high-pressure CrP₂, isolated from the crushed, central single-crystal region of the high-pressure compacts described above, were examined

with a Buerger precession camera using Mo *K* α radiation. They show monoclinic symmetry with lattice constants given above (Table 1). The only conditions for systematically absent reflections are $h+k=2n+1$ and possible space groups are accordingly *C2*, *Cm*, *C2/m*. The similarity in unit-cell dimensions and composition suggested a structure like that found for OsGe₂ (Weitz, Born & Hellner, 1960) or that described for NbAs₂ by Furu- seth & Kjekshus (1965a). The two structures are essentially the same although they have been described in

Table 2. *Evaluation of Guinier-Hägg patterns of CrP₂ and CrAs₂ taken with Cu K α radiation*

| CrP ₂ | | | | | CrAs ₂ | | | | |
|------------------|----------------|----------------|----------------|----------------|-------------------|----------------|----------------|----------------|----------------|
| hkl | d _c | d _o | I _c | I _o | hkl | d _c | d _o | I _c | I _o |
| 001 | 6.1796 | 6.1798 | 9 | w | 001 | 6.4068 | - | 0 | - |
| -201 | 4.0863 | 4.0865 | 38 | s | -201 | 4.4151 | 4.4133 | 5 | vw |
| 200 | 3.5752 | 3.5750 | 10 | w | 200 | 3.8554 | 3.8526 | 2 | vw |
| -202 | 3.2632 | 3.2632 | 10 | w | -202 | 3.4493 | - | 0 | - |
| 002 | 3.0898 | - | 1 | - | 002 | 3.2034 | 3.2021 | 11 | w |
| 110 | 2.7930 | 2.7919 | 14 | w | 110 | 3.0128 | 3.0125 | 2 | vw |
| -111 | 2.7512 | 2.7499 | 9 | vw | -111 | 2.9571 | 2.9569 | 6 | vw |
| 201 | 2.5910 | 2.5888 | 3 | vw | 201 | 2.7527 | 2.7521 | 4 | vw |
| 111 | 2.3793 | 2.3782 | 100 | vvs | 111 | 2.5425 | 2.5428 | 100 | vvs |
| -203 | 2.3550 | 2.3555 | 24 | m | -203 | 2.4579 | 2.4579 | 28 | s |
| -112 | 2.3039 | 2.3032 | 18 | m | -112 | 2.4450 | 2.4450 | 33 | s |
| 003 | 2.0599 | 2.0597 | 30 | s | -402 | 2.2076 | 2.2075 | 25 | m |
| -402 | 2.0432 | 2.0433 | 10 | w | -311 | 2.1896 | 2.1896 | 43 | vs |
| -311 | 2.0242 | 2.0238 | 19 | m | -401 | 2.1678 | 2.1676 | 4 | vw |
| -401 | 1.9998 | 2.0011 | 11 | w | 003 | 2.1356 | 2.1354 | 23 | m |
| -312 | 1.9772 | 1.9770 | 31 | s | -312 | 2.1264 | 2.1266 | 14 | w |
| 202 | 1.9172 | - | 0 | - | 310 | 2.0215 | 2.0216 | 22 | m |
| 112 | 1.8984 | 1.8978 | 34 | s | 202 | 2.0187 | - | 1 | - |
| -403 | 1.8851 | 1.8857 | 22 | m | -403 | 2.0148 | 2.0150 | 14 | w |
| 310 | 1.8743 | 1.8740 | 38 | s | 112 | 2.0082 | 2.0082 | 18 | m |
| -113 | 1.8347 | 1.8346 | 23 | m | -113 | 1.9284 | - | 8 | s |
| 400 | 1.7876 | 1.7878 | 27 | s | 400 | 1.9277 | 1.9278 | 30 | s |
| -204 | 1.7703 | 1.7696 | 13 | w | -313 | 1.8816 | 1.8818 | 37 | s |
| -313 | 1.7680 | 1.7680 | 37 | s | -204 | 1.8389 | 1.8392 | 6 | vw |
| -404 | 1.6316 | - | 0 | - | 311 | 1.7419 | - | 1 | - |
| 311 | 1.6272 | - | 0 | - | -404 | 1.7247 | - | 1 | - |
| 004 | 1.5449 | - | 1 | - | 020 | 1.6365 | 1.6366 | 28 | s |
| 401 | 1.5282 | - | 4 | - | 401 | 1.6349 | - | 2 | - |
| 113 | 1.5238 | - | 0 | - | 004 | 1.6017 | - | 0 | - |
| 020 | 1.5170 | 1.5164 | 28 | s | 113 | 1.6014 | - | 1 | - |
| -314 | 1.5137 | - | 5 | - | -314 | 1.5962 | - | 2 | - |
| 203 | 1.4948 | 1.4951 | 19 | m | 021 | 1.5856 | - | 0 | - |
| -114 | 1.4775 | 1.4780 | 4 | vw | 203 | 1.5664 | 1.5664 | 16 | m |
| 021 | 1.4733 | - | 0 | - | -512 | 1.5625 | 1.5625 | 4 | vw |
| -512 | 1.4439 | 1.4442 | 8 | vw | -114 | 1.5443 | 1.5443 | 17 | m |
| -221 | 1.4222 | - | 4 | - | -221 | 1.5345 | - | 0 | - |
| -513 | 1.4152 | 1.4140 | 4 | vw | -513 | 1.5240 | 1.5243 | 3 | vw |
| -205 | 1.4000 | - | 3 | - | -511 | 1.5121 | 1.5124 | 2 | vw |
| -511 | 1.3969 | - | 0 | - | 220 | 1.5064 | - | 0 | - |
| 220 | 1.3965 | - | 1 | - | -222 | 1.4785 | - | 0 | - |
| -405 | 1.3838 | - | 0 | - | -602 | 1.4730 | - | 0 | - |
| 312 | 1.3827 | - | 1 | - | -603 | 1.4717 | - | 0 | - |
| -222 | 1.3756 | - | 2 | - | 312 | 1.4694 | 1.4693 | 9 | vw |
| -603 | 1.3621 | - | 0 | - | 022 | 1.4573 | 1.4577 | 3 | vw |
| 022 | 1.3617 | - | 0 | - | -205 | 1.4515 | - | 3 | - |
| -602 | 1.3587 | - | 2 | - | -405 | 1.4513 | 1.4515 | 4 | vw |
| -514 | 1.3231 | - | 0 | - | -514 | 1.4139 | 1.4140 | 5 | vw |
| 221 | 1.3091 | - | 1 | - | 221 | 1.4067 | - | 1 | - |
| -604 | 1.3034 | 1.3032 | 7 | vw | -601 | 1.4019 | 1.4020 | 2 | vw |
| 402 | 1.2955 | 1.2951 | 2 | vw | -604 | 1.3986 | 1.3987 | 5 | vw |
| -601 | 1.2946 | - | 1 | - | 510 | 1.3951 | 1.3952 | 5 | vw |
| 510 | 1.2936 | 1.2935 | 4 | vw | 402 | 1.3763 | - | 0 | - |
| | | | | | -223 | 1.3622 | 1.3622 | 11 | w |
| | | | | | -315 | 1.3469 | 1.3470 | 3 | vw |
| | | | | | -422 | 1.3147 | 1.3145 | 12 | w |
| | | | | | 114 | 1.3123 | 1.3124 | 4 | vw |
| | | | | | -421 | 1.3061 | - | 2 | - |
| | | | | | 023 | 1.2990 | 1.2993 | 12 | vw |

Table 4. *Positional and thermal parameters of CrP₂*

Numbers in parenthesis are e.s.d.'s in the least significant digit.

| | <i>C2/m</i> | <i>x</i> | <i>y</i> | <i>z</i> | <i>B</i> (Å ²) |
|------|---------------|------------|----------|------------|----------------------------|
| Cr | 4(<i>i</i>) | 0.8426 (1) | 0 | 0.2958 (1) | 0.21 (2) |
| P(1) | 4(<i>i</i>) | 0.6017 (2) | 0 | 0.4005 (2) | 0.36 (2) |
| P(2) | 4(<i>i</i>) | 0.1437 (2) | 0 | 0.0288 (2) | 0.34 (2) |

In the refinement in space group *C2* the *y* coordinates are no longer fixed by symmetry. Thus the two *y* parameters of the P atoms were varied while the *y* coordinate of Cr was held constant to fix the origin of the unit cell. This refinement when compared with the refinement in *C2/m* resulted in only insignificant differences in positional parameters: the *y* parameters of the P atoms differed by 0.002 ± 0.006 and 0.001 ± 0.004 from the corresponding parameter in the centrosymmetric space group. Thus the space group of CrP₂ is within the (relatively high) accuracy of the data clearly *C2/m*.

Discussion of the CrP₂ Structure

The densities of the new high-pressure CrP₂ and CrAs₂ phases are plotted in Fig. 1 together with the densities of normal-pressure compounds in the respective binary systems. The new phases have higher densities than the phases with adjacent compositions. This is in accord with their occurrence at high pressures.

A stereo view of the CrP₂ structure drawn with the aid of Johnson's (1965) program is shown in Fig. 2. A parallel projection of the structure along the *y* axis is given in Fig. 3. The nearest-neighbor environments of CrP₂ (Table 5, Fig. 4) when compared with those of high-pressure CrP₄ (Jeitschko & Donohue, 1972) show higher coordination for all atoms. In CrP₄ the Cr atom is in octahedral P coordination; in CrP₂ it is eight-coordinated to P with six atoms forming a trigonal prism plus two more P atoms outside the rectangular faces. Concurring with the higher coordination number (CN) interatomic distances are larger: the shortest Cr–P distance in CrP₄ is 2.29 Å as compared to 2.35 Å in CrP₂; the six Cr–P distances in CrP₄ average 2.34 Å, while the average distance for the eight Cr–P interactions in CrP₂ is 2.41 Å. In our discussion of bonding in CrP₄ Cr–Cr bonds were assumed across the edges of the edge-sharing [CrP₆] octahedra in or-

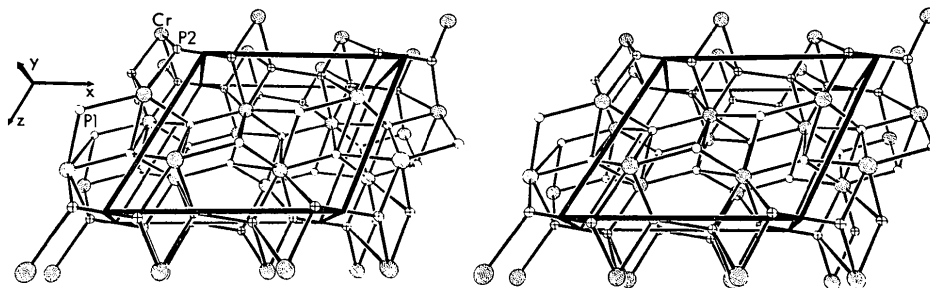
der to explain deviations from ideal bonding angles and its diamagnetic behavior; the Cr–Cr distances in CrP₄ are 3.18 Å. In CrP₂ there are three even-shorter Cr–Cr interactions: 2.78 (1×) and 3.03 Å (2×). The two nonequivalent P atoms in CrP₄ are tetrahedrally coordinated to P and Cr. There are no other neighbors within bonding distance; thus *sp*³ mixing is a good approximation for P in CrP₄. In CrP₂ the P(2) atom is in first approximation also tetrahedrally coordinated to three Cr and one P(2) atom. The P–P distance is 2.189(2) Å, which is within the range of 2.21 ± 0.02 Å found for other P–P bonds (Dahl, 1969) but slightly shorter than the shortest P–P bond of 2.198(1) Å in CrP₄. The bonding angles, however, show considerable deviation from the ideal tetrahedral angle of 109° to make room for two more P atoms at 2.49 Å, thus increasing CN to six. The P(1) atom in CrP₂ has five Cr neighbors forming a distorted square pyramid suggesting *sp*³*d* mixing. This environment is less frequently found for pnictogens (PF₅ and AsF₅ are trigonal bipyramidal). It does occur for P in NbPS (Donohue &

Table 5. *Interatomic distances and angles in the CrP₂ structure*

Standard deviations, computed from e.s.d.'s of positional parameters and lattice constants, are all less than 0.002 Å and 0.2° respectively. All distances less than 3.2 Å are given. Interatomic angles are listed only for the five and four nearest neighbors of P(1) and P(2) respectively.

| | | | |
|------------|---------|------------|-------|
| Cr: 2 P(2) | 2.348 Å | | |
| 1 P(2) | 2.362 | | |
| 2 P(1) | 2.414 | | |
| 1 P(1) | 2.432 | | |
| 2 P(1) | 2.487 | | |
| 1 Cr | 2.777 | | |
| 2 Cr | 3.034 | | |
| P(1): 2 Cr | 2.414 | P(2): 2 Cr | 2.348 |
| 1 Cr | 2.432 | 1 Cr | 2.362 |
| 2 Cr | 2.487 | 1 P(2) | 2.189 |
| 2 P(1) | 2.616 | 2 P(2) | 2.494 |
| 1 P(1) | 2.665 | 2 P(2) | 3.034 |
| 2 P(1) | 3.034 | 2 P(1) | 3.100 |
| 2 P(2) | 3.100 | | |

Cr–P(1)–Cr: 69.0 (2×), 75.2 (1×), 77.9 (1×), 114.1 (2×), 115.8 (2×), 129.2 (2×).
 Cr–P(2)–Cr: 80.5 (1×), 116.0 (2×)
 Cr–P(2)–P(2): 112.5 (1×), 114.2 (2×)

Fig. 2. Stereo drawing of CrP₂ with OsGe₂-type structure.

Bierstedt, 1969) or for As in NbSiAs (Johnson & Jeitschko, 1972). Again the coordination for P(1) in CrP₂ is increased by three more P atoms at distances of 2.62 (2×) and 2.67 (1×) Å, which must be considered as bonding. If two more P atoms at 3.034 Å are also included (not shown in Figure 4), the coordination of the P(1) atom becomes a very distorted bicapped tetragonal prism (not a bicapped antiprism, which is found more frequently for CN 10).

Considering only short near-neighbor metal-nonmetal interactions, there are $\frac{1}{2}$ bonds per formula unit CrP₂: $\frac{8}{2}$ for Cr, $\frac{5}{2}$ for P(1), and (including one P-P bond) $\frac{4}{2}$ for P(2). On the other hand, there are only 16 valence electrons per formula unit, a deficit of 1 electron if two-electron bonds were assumed. If Cr-Cr and additional P-P interactions – at least some of which are undoubtedly bonding – are also included the electron deficit becomes even greater. This lack of bonding electrons is of course characteristic of metals and intermetallic compounds. The near-neighbor environments in CrP₂ may therefore be considered as the result of a

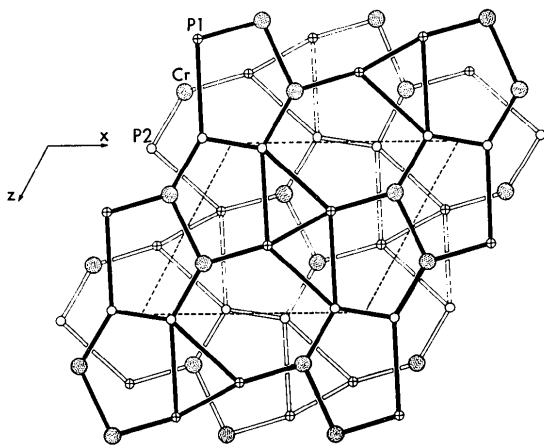


Fig. 3. Projection of CrP₂ with OsGe₂-type structure. Atoms at $y=0$ are connected by full lines and atoms at $y=\frac{1}{2}$ are connected by double lines.

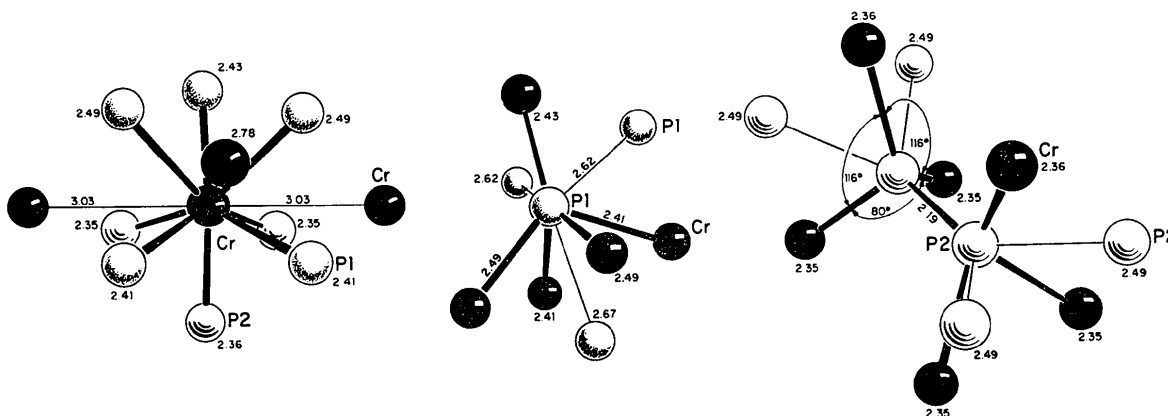


Fig. 4. Near-neighbor environments in CrP₂.

compromise between directional covalent and delocalized metallic bonding.

The known compounds with OsGe₂ or NbAs₂ type structure are listed in Table 6. As has been mentioned above, the atomic arrangement is essentially the same in both structures. The OsGe₂ structure has been refined in space group $C2/m$ while space group $C2$ was chosen for the refinement of NbAs₂. The quality of the intensity data available for the refinement of NbAs₂, however, was not high enough to unambiguously prove the lower symmetry. Unequivocal evidence for space group $C2$ in some of the compounds of Table 6 would strongly suggest diffusionless phase transitions $C2 \rightarrow C2/m$ upon heating. For the purpose of the following discussion, however, the question of space group is not important and for simplicity we will refer to the compounds of Table 6 as OsGe₂ type compounds.

Table 6. Occurrence of OsGe₂ (NbAs₂)-type compounds

| | | | | |
|---------------------------------|--------------------------------------|----------------------------------|--|---------------------------------|
| VP ₂ ¹ | VAs ₂ ^{1,3} | CrP ₂ [*] | CrAs ₂ [*] | OsGe ₂ ¹² |
| NbP ₂ ^{1,2} | NbAs ₂ ^{4,5,6,8} | NbSb ₂ ^{6,8} | MoAs ₂ ^{1,9,10,11} | |
| TaP ₂ ^{1,2} | TaAs ₂ ^{4,5,7} | TaSb ₂ ^{1,7} | α-WP ₂ ^{1,2} | |

References: *This work, 1: Hulliger (1964), 2: Rundqvist (1966), 3: Meissner & Schubert (1965), 4: Furuseth & Kjekshus (1965a), 5: Saini, Calvert & Taylor (1964), 6: Furuseth & Kjekshus (1964a), 7: Furuseth & Kjekshus (1965b), 8: Furuseth & Kjekshus (1964b), 9: Brown (1965), 10: Taylor, Calvert & Hunt (1965), 11: Jensen, Kjekshus & Skansen (1966), 12: Weitz, Born & Hellner (1960).

Crystal chemistry of transition metal dipnictides

Some 25 structure types have been described for compositions TM₂, where T is a transition metal from the titanium group to the nickel group and M is an element from the silicon, phosphorus, or sulfur group of the Periodic Table. About ten of them are represented by

transition metal dipnictides.* These dipnictide structures may be divided into two main groups with distinct differences in structural characteristics:

(a) *Dipnictides with low-coordination structures*

These are the dipnictides with marcasite (*e.g.*, FeP₂ and homologous compounds,† pyrite (*e.g.*, PdAs₂, PtSb₂), arsenopyrite (*e.g.*, RhP₂, CoAs₂), and paramelsbergite (NiAs₂; Fleet, 1972) structures. In these compounds the transition metal is always octahedrally coordinated by pnictogen while the pnictogen atoms are tetrahedrally surrounded by three metal atoms and one pnictogen atom, thus forming pairs. The PdP₂-type diphosphides (NiP₂, PdP₂) can also be assigned to this family, although their coordinations are somewhat different: the metal atom is situated in a square of P atoms while the P atom is tetrahedrally coordinated to two metal and two P atoms.

(b) *Dipnictides with high-coordination structures*

This group consists of compounds‡ with the following structure types: CuAl₂ (TiSb₂, VSb₂), TiAs₂ (TiAs₂, ZrSb₂, HfSb₂), PbCl₂ (TiP₂, ZrP₂, HfP₂, ZrAs₂, HfAs₂), OsGe₂ (Table 6), and MoP₂ (MoP₂, WP₂). The near-neighbor environments of these structures show the tendency for high coordination with no sharp distinction between nearest and second nearest neighbors, as was discussed above for CrP₂. The CuAl₂ and TiAs₂-type structures do not occur for phosphides, apparently because of the unfavorable radius ratio. Their coordinations are also somewhat different from those of the other three structure types of this group.

The environment of the metal in the dipnictides with PbCl₂, OsGe₂, and MoP₂-type structures is a trigonal prism of pnictogen atoms with three additional pnictogen atoms (PbCl₂ type), or two additional pnictogen plus one metal atom (OsGe₂ type), or one additional pnictogen plus two metal atoms (MoP₂ type) outside the three rectangular faces of the prism. Two additional metal atoms outside the triangular faces of the prism increase CN to 11. Thus although the overall CN of the metal atom is the same in the three types, the number of pnictogen atoms around the metal atom is decreasing from nine in ZrP₂, to eight in NbP₂, to seven in MoP₂, while the metal coordination is increasing correspondingly. This regularity may be rationalized considering the change in electronegativity which results in larger electrostatic repulsion for metal-metal bonding in ZrP₂ as compared to metal-metal bonding in MoP₂. There are two different pnictogen atoms in these three structure types: one, for which the nearest neighbor environ-

ment is essentially tetrahedral, and the other with square pyramidal configuration. The systematic coordination change of the metal atom is reflected in the changing coordination of the pnictogen atoms: in ZrP₂ both the tetrahedral and the square pyramidal P have only Zr nearest neighbors; in NbP₂ the square pyramidal P has as closest neighbors only Nb atoms, while the tetrahedral P has three P plus one Nb; in MoP₂ finally both P atoms have one close P neighbor. As has been emphasized above for CrP₂, there are further near neighbors within bonding distances in all these pnictogen coordinations.

Besides their striking differences in coordinations the two groups of dipnictide structures differ also in other respects. The structures of the low-coordinated dipnictides (pyrite and marcasite) are common also for numerous dichalcogenides while the high-coordinated dipnictide structures occur also for disilicides, digermanides, and distannides. Thus the PbCl₂-type structure is not only found for TiP₂, ZrAs₂ *etc.*, but also for isoelectronic MoGe₂; OsGe₂ is isostructural and isoelectronic with CrP₂, MoAs₂, *etc.*; the CuAl₂ type occurs not only for TiSb₂ and VSb₂ but also for FeGe₂ and FeSn₂.

The transition metals of the high-coordinated dipnictides are always from the Ti, V, or Cr group of the Periodic Table, while they are from the Fe, Co, or Ni group for the low-coordinated dipnictides. No dipnictides have been reported with transition metals from the Mn group. The higher CN for dipnictides of the earlier transition metals is certainly not only a radius ratio effect since V and Cr are smaller than the platinum metals.

Bonding for compounds with the pyrite, marcasite, and arsenopyrite structures has been discussed extensively (Hulliger & Mooser, 1965; Kjekshus & Nicholson, 1971; Goodenough, 1972) and metallic or semiconducting behavior in these structures can be predicted on the basis of the generalized (8 - *N*) rule (see *e.g.*, Mooser & Pearson, 1960; Hulliger & Mooser, 1963; Pearson, 1964). Sometimes this rule has also been used inappropriately for compounds described here as high-coordinated dipnictides. The square pyramidal pnictogen coordination found in all high-coordinated dipnictide structures strongly suggests participation of the pnictogen *d* orbitals in bonding (*sp*³*d* hybridization). This can be understood considering the smaller electroaffinity of the group IV, V, and VI transition metals as compared to the iron and platinum group metals. With the filling of pnictogen *d*-states the octet rule is no longer applicable. As was shown above for CrP₂, the number of valence electrons in these structures is smaller than the number of bonding states deduced from the nearest-neighbor environments. Thus the metallic conductivity found for all high-coordinated dipnictides is rationalized.

We are indebted to C. G. Frederick and J. L. Gillson for communicating results on magnetic and elec-

* The words *pnictogen* and *pnictide* are used to denote the group VA elements and compounds in which they are the more electronegative component.

† References may be found in the compilation of Pearson (1967) and the reviews by Hulliger (1968), Lundström (1968), and Ward (1972).

‡ This account excludes structures which occur for bismuthides only.

tric conductivity measurements, C. L. Hoover for supervision of the high-pressure reactions, W. H. O'Connor for competent help in sample preparation, and D. M. Graham for enthusiastic support at several stages of the crystallographic work.

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