

Refinement of the Crystal Structure of Hf₂P

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The crystal structure of Hf₂P is isotypic with that of Ta₂P. The structure of Hf₂P was refined using single-crystal X-ray data and least squares fitting of the parameters to these data.

The interatomic distances in Hf₂P, Ti₂S and Ta₂P are classified and discussed. It is shown that the space filling of six different representatives of the Ta₂P type structure decreases as the radius ratio increases.

The crystal structure of Ta₂P was recently determined at this Institute by Nylund.¹ At the same time and independently the crystal structure of the isotypic compound Ti₂S was solved by Owens, Conard and Franzen.² The existence of a further isotypic compound in the Hf—P system was also recently reported.³ Thus it appeared interesting to compare in detail the interatomic distances in these three compounds. This paper reports the result of a least squares refinement of the structure of Hf₂P.

EXPERIMENTAL

Purities of chemicals and the method of preparation have already been described in an earlier paper.³ Single-crystals large enough for the X-ray investigations were grown by heat-treatment for 40 days at 1150°C. The sample, which had the nominal composition Hf₂P, also contained traces of Hf₃P.

The cell dimensions were determined with a Guinier-Hägg camera using CrK α_1 radiation of wavelength 2.28962 Å and silicon as internal calibration standard ($a=5.43054$ Å).

The intensities were measured on the Weissenberg recordings of the zero and first layer lines, perpendicular to the short c -axis. Each layer was recorded on four films, with iron foil absorbers interleaved with successive films, and using Zr-filtered molybdenum K α radiation. The visual estimation of the intensities was performed with an intensity scale obtained from a successive increase in the exposure of one of the reflexions from the same crystal. The crystal used was fairly well-formed, but a somewhat idealized shape had to be used when applying the absorption correction. The approximate size of the crystal was $0.027 \times 0.014 \times 0.12$ mm with the rotation axis along the needle-axis. The calculated linear absorption coefficient ⁴ was 748 cm^{-1} .

REFINEMENT OF THE Hf_2P STRUCTURE

The dimensions of the orthorhombic unit cell, as determined from a powder photograph of the sample from which the single-crystal was selected, were as follows:

$$a = 15.031 \text{ \AA} \quad b = 12.258 \text{ \AA} \quad c = 3.5738 \text{ \AA}$$

The standard deviations were throughout less than 1:7500. The observed systematic extinctions

$$\begin{aligned} h0l \text{ absent for } h + l = 2n + 1 \text{ and} \\ 0kl \text{ absent for } k + l = 2n + 1 \end{aligned}$$

were in complete agreement with those observed for Ta_2P . Thus the centrosymmetric space group $Pn\bar{n}m$ was used for the description of the structure.

Lp and absorption corrections were applied, using program 2 in Table 1, which presents all computer programs used in this investigation. The coordinates of the atoms in Ta_2P reported by Nylund,¹ together with estimated values for the scale and temperature factors, were used as the starting parameters in the least squares refinement. Scattering factors were obtained from Ref. 4 while the real part of the anomalous dispersion correction used was taken from Ref. 5.

The reflexions were weighted according to the scheme

$$w = 1/(a + |F_o| + c|F_o|^2)$$

proposed by Cruickshank *et al.*⁶ After some adjustments, based on weight analyses after each refinement cycle, the finally chosen value of a was 110 and that of c 0.008. A weight analysis from the last cycle is presented in Table 3.

The discrepancy index, defined as

$$R = \sum ||F_o| - |F_c|| / \sum |F_o|$$

Table 1. Computer programs used for the crystallographic calculations on the CD 3600 computer in Uppsala (all programs written in FORTRAN IV).

| Program performing | Authors |
|---|---|
| 1. Least squares refinement of unit cell dimensions. | J. Tegenfeldt, Uppsala, Sweden. |
| 2. Lorentz-polarization, absorption and extinction corrections. | P. Coppens, L. Leiserowitz and D. Rabinovich, Rehovoth, Israel; modified by O. Olofsson and M. Elfström, Uppsala and (incorporation of extinction correction) by B. Brandt and S. Åsbrink, Stockholm, Sweden. |
| 3. Least squares refinement of positional parameters and temperature factors. | P. K. Gantzel, R. A. Sparks and K. N. Trueblood, Los Angeles, U.S.A.; modified by A. Zalkin, Berkeley, U.S.A. and by C.-I. Brändén, R. Liminga and J.-O. Lundgren, Uppsala, Sweden. |
| 4. Fourier summations and structure factor calculations. | A. Zalkin, Berkeley, U.S.A.; modified by R. Liminga and J.-O. Lundgren, Uppsala, Sweden. |
| 5. Interatomic distances. | A. Zalkin, Berkeley, U.S.A. |

Table 2. Final structural data for Hf₂P. Space group *Pnmm* (No. 58). All atoms in position 4(*g*). *Z* = 12. *a* = 15.031 Å, *b* = 12.258 Å, and *c* = 3.5738 Å. Cell volume 658.5 Å³.

| Atom | Position | Positional parameters and standard deviations | | | | Temp. factors and st. dev. | |
|-------|---------------|---|-------------|----------|-------------|----------------------------|-------------|
| | | <i>x</i> | $\sigma(x)$ | <i>y</i> | $\sigma(y)$ | <i>B</i> | $\sigma(B)$ |
| Hf(1) | 4(<i>g</i>) | 0.08502 | 0.00015 | 0.11717 | 0.00020 | 0.206 | 0.028 |
| Hf(2) | 4(<i>g</i>) | 0.29053 | 0.00016 | 0.18831 | 0.00019 | 0.177 | 0.027 |
| Hf(3) | 4(<i>g</i>) | 0.10554 | 0.00016 | 0.52537 | 0.00019 | 0.202 | 0.026 |
| Hf(4) | 4(<i>g</i>) | 0.24591 | 0.00016 | 0.90383 | 0.00020 | 0.283 | 0.029 |
| Hf(5) | 4(<i>g</i>) | 0.47851 | 0.00018 | 0.83744 | 0.00023 | 0.445 | 0.033 |
| Hf(6) | 4(<i>g</i>) | 0.42351 | 0.00015 | 0.41212 | 0.00019 | 0.079 | 0.025 |
| P(1) | 4(<i>g</i>) | 0.1480 | 0.0012 | 0.3130 | 0.0015 | 0.63 | 0.25 |
| P(2) | 4(<i>g</i>) | 0.2871 | 0.0012 | 0.5562 | 0.0015 | 0.51 | 0.23 |
| P(3) | 4(<i>g</i>) | 0.0906 | 0.0009 | 0.7554 | 0.0012 | 0.01 | 0.16 |

from the last cycle was 9.7 % (including all 717 observed reflexions) and the shifts were then less than 2 % of the calculated standard deviations for all parameters. The final atomic and thermal parameters are given in Table 2. The (absorption-corrected) observed and calculated structure factors are presented in Table 4. No extinction correction was applied.

The temperature factors of Table 2 show a divergence which is rather large compared with the calculated standard deviations. Any physical interpretation of this fact would hardly be significant, since, as mentioned before, there is some uncertainty in the absorption correction applied.

A final difference synthesis showed positive and negative regions, which in no case exceeded 20 % of the phosphorus peaks in the *F_o* synthesis.

Table 5 shows the interatomic distances together with their standard deviations.

Table 3. Weight analysis from the last cycle of refinement. $\Delta = ||F_o| - |F_c||$

| Interval <i>F_o</i> | $\overline{w \cdot \Delta^2}$ (normalized) | Number of reflexions | Interval $\sin \theta$ | $\overline{w \cdot \Delta^2}$ (normalized) | Number of reflexions |
|-------------------------------|---|----------------------|------------------------|---|----------------------|
| 0.0—96.4 | 1.41 | 71 | 0.00—0.46 | 0.47 | 341 |
| 96.4—116.3 | 1.22 | 72 | 0.46—0.58 | 0.78 | 154 |
| 116.3—132.5 | 1.07 | 72 | 0.58—0.67 | 0.93 | 73 |
| 132.5—144.1 | 0.88 | 71 | 0.67—0.74 | 1.16 | 43 |
| 144.1—160.8 | 1.04 | 72 | 0.74—0.79 | 0.55 | 28 |
| 160.8—176.6 | 0.61 | 72 | 0.79—0.84 | 0.89 | 25 |
| 176.6—206.8 | 1.26 | 71 | 0.84—0.89 | 1.23 | 19 |
| 206.8—237.0 | 0.80 | 72 | 0.89—0.93 | 1.00 | 19 |
| 237.0—294.3 | 0.68 | 72 | 0.93—0.97 | 0.92 | 10 |
| 294.3—725.3 | 1.04 | 72 | 0.97—1.00 | 2.09 | 5 |

Table 4. Observed and calculated structure factors. The observed structure factors are corrected for absorption.

| h k l F _o F _c | | | | h k l F _o F _c | | | | h k l F _o F _c | | | | h k l F _o F _c | | | | | | | | | | | | | |
|---|---|----|---|---|-------|---|----|---|-------|-------|----|---|---|-------|-------|---|----|---|-------|-------|----|----|---|-------|-------|
| 0 | 0 | 4 | 0 | 392.4 | 458.7 | 8 | 6 | 0 | 110.5 | 109.3 | 17 | 11 | 0 | 220.8 | 177.2 | 2 | 5 | 1 | 133.7 | 110.7 | 10 | 8 | 1 | 375.7 | 419.4 |
| 0 | 0 | 8 | 0 | 103.3 | 81.0 | 8 | 8 | 0 | 379.3 | 405.7 | 17 | 12 | 0 | 228.1 | 205.0 | 2 | 6 | 1 | 165.2 | 156.4 | 10 | 9 | 1 | 102.3 | 92.4 |
| 0 | 0 | 10 | 0 | 325.7 | 348.5 | 8 | 6 | 0 | 67.5 | 64.5 | 17 | 14 | 0 | 327.3 | 303.8 | 2 | 7 | 1 | 343.3 | 354.1 | 10 | 12 | 1 | 207.5 | 194.5 |
| 0 | 0 | 12 | 0 | 189.3 | 200.2 | 8 | 9 | 0 | 145.9 | 143.6 | 17 | 21 | 0 | 132.8 | 135.1 | 2 | 9 | 1 | 203.6 | 197.7 | 10 | 13 | 1 | 130.7 | 110.9 |
| 0 | 0 | 14 | 0 | 359.5 | 375.3 | 8 | 10 | 0 | 76.1 | 60.2 | 17 | 30 | 0 | 117.3 | 153.2 | 2 | 10 | 1 | 230.3 | 233.9 | 10 | 14 | 1 | 163.9 | 131.1 |
| 0 | 0 | 16 | 0 | 157.9 | 155.7 | 8 | 11 | 0 | 74.7 | 82.2 | 18 | 0 | 0 | 296.1 | 329.4 | 2 | 11 | 1 | 310.8 | 331.9 | 10 | 15 | 1 | 216.9 | 200.3 |
| 0 | 0 | 18 | 0 | 141.4 | 147.0 | 8 | 13 | 0 | 377.7 | 369.7 | 18 | 3 | 0 | 218.8 | 206.5 | 2 | 12 | 1 | 173.0 | 158.7 | 10 | 17 | 1 | 250.9 | 257.1 |
| 0 | 0 | 20 | 0 | 150.3 | 176.7 | 8 | 15 | 0 | 219.8 | 181.9 | 18 | 4 | 0 | 365.6 | 388.8 | 2 | 13 | 1 | 104.9 | 107.5 | 10 | 25 | 1 | 116.6 | 133.3 |
| 0 | 0 | 22 | 0 | 137.2 | 158.1 | 8 | 16 | 0 | 245.9 | 207.5 | 18 | 6 | 0 | 215.9 | 212.5 | 2 | 14 | 1 | 225.9 | 214.6 | 10 | 27 | 1 | 116.9 | 134.2 |
| 0 | 0 | 24 | 0 | 692.2 | 652.7 | 8 | 19 | 0 | 179.9 | 181.9 | 18 | 7 | 0 | 281.4 | 319.9 | 2 | 17 | 1 | 228.2 | 220.3 | 11 | 0 | 1 | 176.7 | 181.7 |
| 0 | 1 | 0 | 0 | 303.5 | 285.8 | 8 | 31 | 0 | 87.2 | 89.2 | 18 | 10 | 0 | 165.5 | 145.7 | 2 | 19 | 1 | 165.5 | 173.4 | 11 | 1 | 1 | 86.4 | 70.8 |
| 0 | 1 | 2 | 0 | 287.6 | 266.2 | 8 | 31 | 1 | 259.0 | 262.2 | 18 | 12 | 0 | 178.5 | 151.5 | 2 | 21 | 1 | 204.9 | 273.1 | 11 | 3 | 1 | 186.5 | 202.0 |
| 0 | 1 | 4 | 0 | 258.5 | 249.8 | 8 | 31 | 2 | 500.3 | 512.6 | 18 | 17 | 0 | 189.8 | 89.7 | 2 | 22 | 1 | 166.2 | 164.1 | 11 | 4 | 1 | 59.3 | 51.7 |
| 0 | 1 | 6 | 0 | 324.3 | 368.8 | 8 | 31 | 3 | 220.6 | 223.6 | 18 | 25 | 0 | 150.0 | 129.5 | 2 | 24 | 1 | 84.3 | 69.4 | 11 | 6 | 1 | 130.6 | 110.3 |
| 0 | 1 | 8 | 0 | 179.5 | 184.3 | 8 | 31 | 4 | 251.7 | 257.0 | 19 | 1 | 0 | 293.2 | 336.0 | 2 | 25 | 1 | 117.6 | 152.7 | 11 | 7 | 1 | 124.4 | 110.4 |
| 0 | 1 | 10 | 0 | 103.9 | 106.0 | 8 | 31 | 5 | 107.9 | 91.0 | 19 | 7 | 0 | 133.8 | 103.4 | 3 | 3 | 1 | 617.2 | 656.6 | 11 | 8 | 1 | 172.6 | 152.6 |
| 0 | 1 | 12 | 0 | 225.2 | 297.2 | 8 | 31 | 6 | 140.5 | 126.1 | 19 | 9 | 0 | 220.6 | 210.9 | 3 | 4 | 1 | 87.7 | 84.0 | 11 | 9 | 1 | 267.1 | 265.6 |
| 0 | 1 | 14 | 0 | 242.3 | 248.8 | 8 | 31 | 7 | 87.2 | 69.9 | 19 | 11 | 0 | 150.8 | 202.1 | 3 | 5 | 1 | 48.6 | 26.4 | 11 | 11 | 1 | 107.0 | 85.7 |
| 0 | 1 | 16 | 0 | 137.2 | 125.0 | 8 | 31 | 8 | 127.1 | 120.2 | 19 | 13 | 0 | 146.6 | 106.6 | 3 | 6 | 1 | 133.1 | 116.3 | 11 | 13 | 1 | 218.2 | 203.2 |
| 0 | 1 | 18 | 0 | 180.9 | 158.0 | 8 | 31 | 9 | 252.1 | 251.6 | 19 | 19 | 0 | 219.6 | 219.3 | 3 | 7 | 1 | 635.8 | 755.2 | 11 | 15 | 1 | 118.0 | 79.7 |
| 0 | 1 | 20 | 0 | 85.6 | 55.3 | 8 | 31 | 10 | 89.1 | 76.2 | 20 | 4 | 0 | 166.0 | 172.3 | 3 | 8 | 1 | 122.7 | 92.9 | 11 | 14 | 1 | 152.7 | 130.1 |
| 0 | 1 | 22 | 0 | 110.3 | 96.6 | 8 | 31 | 11 | 199.6 | 193.2 | 20 | 11 | 0 | 239.2 | 247.0 | 3 | 9 | 1 | 355.2 | 331.8 | 11 | 15 | 1 | 188.1 | 188.7 |
| 0 | 1 | 24 | 0 | 263.0 | 266.3 | 8 | 31 | 12 | 133.2 | 128.5 | 20 | 12 | 0 | 141.6 | 121.0 | 3 | 10 | 1 | 137.7 | 129.8 | 11 | 16 | 1 | 177.4 | 157.3 |
| 0 | 1 | 26 | 0 | 364.3 | 381.2 | 8 | 31 | 13 | 168.5 | 164.9 | 20 | 15 | 0 | 185.6 | 145.4 | 3 | 11 | 1 | 64.1 | 55.3 | 11 | 17 | 1 | 122.1 | 68.3 |
| 0 | 1 | 28 | 0 | 142.3 | 134.0 | 8 | 31 | 14 | 139.3 | 145.2 | 20 | 17 | 0 | 175.9 | 142.2 | 3 | 12 | 1 | 145.1 | 139.7 | 11 | 19 | 1 | 151.9 | 129.1 |
| 0 | 1 | 30 | 0 | 218.0 | 198.2 | 8 | 31 | 15 | 109.9 | 347.5 | 20 | 19 | 0 | 178.9 | 145.6 | 3 | 13 | 1 | 201.6 | 215.0 | 11 | 21 | 1 | 118.6 | 114.4 |
| 0 | 1 | 32 | 0 | 211.3 | 199.9 | 8 | 31 | 16 | 156.1 | 163.0 | 20 | 25 | 0 | 141.5 | 150.7 | 3 | 14 | 1 | 158.5 | 181.9 | 11 | 23 | 1 | 211.9 | 230.9 |
| 0 | 1 | 34 | 0 | 285.7 | 271.8 | 8 | 31 | 17 | 96.2 | 92.1 | 21 | 3 | 0 | 224.7 | 222.9 | 3 | 15 | 1 | 144.1 | 176.3 | 12 | 1 | 1 | 98.6 | 99.1 |
| 0 | 1 | 36 | 0 | 104.7 | 87.4 | 8 | 31 | 18 | 97.6 | 92.1 | 21 | 6 | 0 | 252.9 | 271.6 | 4 | 1 | 1 | 674.1 | 509.2 | 12 | 2 | 1 | 274.1 | 220.7 |
| 0 | 1 | 38 | 0 | 257.9 | 249.9 | 8 | 31 | 19 | 109.9 | 99.6 | 21 | 8 | 0 | 146.8 | 145.8 | 4 | 2 | 1 | 725.2 | 616.9 | 12 | 3 | 1 | 118.6 | 157.7 |
| 0 | 1 | 40 | 0 | 222.4 | 240.1 | 8 | 31 | 20 | 383.2 | 380.8 | 21 | 16 | 0 | 206.8 | 161.7 | 4 | 3 | 1 | 131.2 | 105.2 | 12 | 4 | 1 | 105.2 | 87.0 |
| 0 | 1 | 42 | 0 | 146.9 | 133.6 | 8 | 31 | 21 | 135.8 | 137.3 | 22 | 0 | 0 | 244.3 | 282.9 | 4 | 4 | 1 | 155.9 | 148.1 | 12 | 5 | 1 | 266.6 | 295.3 |
| 0 | 1 | 44 | 0 | 123.6 | 139.9 | 8 | 31 | 22 | 178.5 | 134.2 | 22 | 11 | 0 | 195.9 | 163.5 | 4 | 5 | 1 | 81.6 | 67.5 | 12 | 7 | 1 | 155.4 | 143.2 |
| 0 | 1 | 46 | 0 | 484.7 | 512.7 | 8 | 31 | 23 | 161.4 | 186.2 | 22 | 12 | 0 | 151.2 | 109.3 | 4 | 6 | 1 | 176.2 | 183.6 | 12 | 9 | 1 | 155.4 | 143.2 |
| 0 | 1 | 48 | 0 | 148.5 | 142.4 | 8 | 31 | 24 | 98.5 | 88.2 | 22 | 16 | 0 | 192.0 | 155.0 | 4 | 7 | 1 | 155.9 | 148.1 | 12 | 11 | 1 | 278.6 | 299.4 |
| 0 | 1 | 50 | 0 | 167.3 | 188.7 | 8 | 31 | 25 | 172.3 | 166.0 | 23 | 1 | 0 | 214.7 | 175.3 | 4 | 8 | 1 | 231.0 | 249.6 | 12 | 12 | 1 | 151.4 | 126.5 |
| 0 | 1 | 52 | 0 | 169.5 | 163.2 | 8 | 31 | 26 | 164.4 | 146.2 | 23 | 2 | 0 | 146.4 | 165.7 | 4 | 9 | 1 | 81.6 | 84.6 | 12 | 13 | 1 | 169.6 | 137.8 |
| 0 | 1 | 54 | 0 | 169.6 | 147.8 | 8 | 31 | 27 | 164.5 | 177.6 | 23 | 3 | 0 | 149.5 | 157.6 | 4 | 10 | 1 | 82.7 | 126.3 | 12 | 14 | 1 | 166.3 | 119.2 |
| 0 | 1 | 56 | 0 | 335.2 | 320.9 | 8 | 31 | 28 | 231.4 | 92.1 | 23 | 4 | 0 | 167.0 | 125.6 | 4 | 11 | 1 | 101.7 | 99.3 | 12 | 15 | 1 | 132.1 | 101.2 |
| 0 | 1 | 58 | 0 | 484.7 | 484.7 | 8 | 31 | 29 | 231.4 | 146.2 | 23 | 6 | 0 | 219.1 | 156.3 | 4 | 12 | 1 | 81.2 | 81.8 | 12 | 17 | 1 | 118.6 | 114.4 |
| 0 | 1 | 60 | 0 | 122.0 | 101.8 | 8 | 31 | 30 | 237.1 | 247.9 | 23 | 8 | 0 | 172.3 | 148.4 | 4 | 13 | 1 | 53.8 | 45.2 | 12 | 19 | 1 | 181.9 | 165.6 |
| 0 | 1 | 62 | 0 | 216.1 | 212.0 | 8 | 31 | 31 | 161.1 | 165.8 | 24 | 0 | 0 | 211.4 | 202.4 | 4 | 14 | 1 | 478.2 | 453.5 | 13 | 1 | 1 | 335.4 | 345.3 |
| 0 | 1 | 64 | 0 | 187.1 | 187.1 | 8 | 31 | 32 | 372.7 | 374.4 | 24 | 4 | 0 | 169.1 | 156.2 | 4 | 15 | 1 | 74.7 | 66.3 | 13 | 2 | 1 | 224.2 | 211.6 |
| 0 | 1 | 66 | 0 | 269.2 | 269.2 | 8 | 31 | 33 | 233.2 | 261.0 | 24 | 6 | 0 | 206.9 | 203.1 | 4 | 16 | 1 | 133.7 | 130.8 | 13 | 3 | 1 | 62.0 | 42.6 |
| 0 | 1 | 68 | 0 | 226.2 | 205.2 | 8 | 31 | 34 | 119.1 | 120.9 | 24 | 7 | 0 | 153.0 | 115.6 | 4 | 17 | 1 | 166.6 | 164.9 | 13 | 4 | 1 | 90.7 | 62.5 |
| 0 | 1 | 70 | 0 | 226.2 | 188.3 | 8 | 31 | 35 | 372.7 | 374.4 | 24 | 9 | 0 | 189.3 | 147.1 | 4 | 18 | 1 | 223.8 | 91.4 | 13 | 5 | 1 | 259.3 | 332.2 |
| 0 | 1 | 72 | 0 | 211.0 | 211.7 | 8 | 31 | 36 | 99.3 | 84.3 | 24 | 16 | 0 | 189.3 | 147.1 | 4 | 19 | 1 | 134.2 | 270.8 | 13 | 6 | 1 | 90.7 | 62.5 |
| 0 | 1 | 74 | 0 | 211.0 | 250.3 | 8 | 31 | 37 | 117.2 | 100.7 | 25 | 1 | 0 | 274.2 | 270.6 | 4 | 20 | 1 | 145.3 | 146.4 | 13 | 7 | 1 | 121.9 | 114.8 |
| 0 | 1 | 76 | 0 | 237.0 | 282.8 | 8 | 31 | 38 | 169.8 | 169.6 | 25 | 10 | 0 | 133.4 | 115.9 | 4 | 21 | 1 | 165.0 | 165.9 | 13 | 8 | 1 | 125.9 | 122.2 |
| 0 | 1 | 78 | 0 | 157.3 | 149.9 | 8 | 31 | 39 | 185.9 | 119.2 | 25 | 14 | 0 | 185.9 | 153.2 | 4 | 22 | 1 | 205.2 | 225.5 | 13 | 9 | 1 | 159.8 | 158.8 |
| 0 | 1 | 80 | 0 | 269.2 | 298.6 | 8 | 31 | 40 | 271.9 | 315.1 | 25 | 15 | 0 | 170.3 | 157.8 | 4 | 23 | 1 | 131.2 | 114.1 | 13 | 14 | 1 | 110.1 | 75.5 |
| 0 | 1 | 82 | 0 | 423.9 | 461.8 | 8 | 31 | 41 | 125.6 | 122.0 | 24 | 22 | 0 | 130.6 | 140.9 | 4 | 24 | 1 | 81.9 | 79.8 | 13 | 15 | 1 | 109.2 | 86.3 |
| 0 | 1 | 84 | 0 | 72.5 | 55.2 | 8 | 31 | 42 | 161.4 | 146.2 | 26 | 10 | 0 | 172.1 | 156.3 | 4 | 25 | 1 | 127.4 | 156.9 | 13 | 16 | 1 | 124.3 | 114.4 |
| 0 | 1 | 86 | 0 | 112.3 | 94.2 | 8 | 31 | 43 | 303.0 | 296.5 | 26 | 9 | 0 | 132.9 | 158.7 | 4 | 26 | 1 | 69.6 | 64.8 | 13 | 18 | 1 | 170.2 | 193.5 |
| 0 | 1 | 88 | 0 | 260.9 | 259.0 | 8 | 31 | 44 | 103.5 | 176.1 | 26 | 11 | 0 | 166.2 | 157.4 | 4 | 27 | 1 | 253.4 | 287.3 | 13 | 19 | 1 | 170.4 | 140.4 |
| 0 | 1 | 90 | 0 | 126.4 | 107.0 | 8 | 31 | 45 | 206.7 | 205.5 | 26 | 19 | 0 | 122.5 | 103.1 | 4 | 28 | 1 | 303.5 | 267.5 | 13 | 21 | 1 | 92.5 | 119.7 |
| 0 | 1 | 92 | 0 | 126.4 | 107.0 | 8 | 31 | 46 | 97.9 | 97.7 | 27 | 6 | 0 | 225.9 | 224.5 | 4 | 29 | 1 | 150.3 | 145.1 | 13 | 23 | 1 | 339.6 | 332.2 |
| 0 | 1 | 94 | 0 | 101.3 | 91.6 | 8 | 31 | 47 | 262.6 | 252.8 | 27 | 11 | 0 | 135.5 | 101.0 | 4 | 30 | 1 | 125.7 | 101.0 | 13 | 24 | 1 | 66.4 | 70.9 |
| 0 | 1 | 96 | 0 | 284.8 | 298.7 | 8 | 31 | 48 | 411.7 | 452.7 | 27 | 20 | 0 | 135.4 | 129.0 | 4 | | | | | | | | | |

Table 4. Continued.

| h | k | l | r ₀ | r ₁ | h | k | l | r ₀ | r ₁ | h | k | l | r ₀ | r ₁ | h | k | l | r ₀ | r ₁ | h | k | l | r ₀ | r ₁ | |
|----|----|---|----------------|----------------|----|----|-------|----------------|----------------|----|----|------|----------------|----------------|----|----|-------|----------------|----------------|----|----|-------|----------------|----------------|--|
| 18 | 3 | 1 | 65.9 | 62.6 | 20 | 8 | 1 | 122.9 | 109.5 | 23 | 8 | 1 | 268.7 | 273.2 | 25 | 22 | 1 | 89.9 | 70.4 | 32 | 1 | 1 | 125.2 | 122.8 | |
| 18 | 4 | 1 | 215.3 | 199.6 | 20 | 9 | 1 | 141.3 | 118.3 | 23 | 9 | 1 | 147.7 | 133.9 | 26 | 1 | 1 | 172.7 | 185.5 | 32 | 6 | 1 | 136.6 | 144.4 | |
| 18 | 7 | 1 | 162.9 | 164.6 | 20 | 11 | 1 | 211.0 | 205.3 | 22 | 11 | 1 | 169.3 | 143.8 | 26 | 3 | 1 | 161.5 | 175.9 | 32 | 12 | 1 | 129.0 | 130.3 | |
| 18 | 9 | 1 | 91.4 | 90.8 | 20 | 14 | 1 | 248.3 | 239.9 | 22 | 21 | 1 | 130.9 | 105.8 | 26 | 6 | 1 | 151.7 | 142.0 | 32 | 17 | 1 | 126.0 | 134.2 | |
| 18 | 10 | 1 | 256.6 | 257.3 | 20 | 21 | 1 | 235.7 | 236.11 | 23 | 1 | 1 | 134.2 | 131.0 | 26 | 14 | 1 | 162.3 | 164.3 | 33 | 4 | 1 | 150.3 | 155.6 | |
| 18 | 13 | 1 | 116.5 | 113.9 | 20 | 23 | 1 | 124.2 | 123.5 | 23 | 2 | 1 | 134.8 | 127.5 | 26 | 11 | 1 | 248.2 | 238.2 | 33 | 4 | 1 | 176.6 | 192.0 | |
| 18 | 15 | 1 | 174.3 | 158.0 | 21 | 0 | 1 | 235.6 | 433.7 | 23 | 4 | 1 | 162.6 | 164.9 | 26 | 15 | 1 | 125.7 | 102.6 | 33 | 11 | 1 | 115.1 | 128.2 | |
| 18 | 21 | 1 | 138.4 | 143.2 | 21 | 1 | 137.2 | 123.5 | 23 | 7 | 1 | 98.8 | 79.8 | 26 | 21 | 1 | 126.0 | 122.7 | 33 | 12 | 1 | 123.5 | 116.6 | | |
| 18 | 23 | 1 | 128.9 | 115.1 | 21 | 3 | 1 | 311.6 | 349.5 | 23 | 8 | 1 | 120.5 | 101.7 | 27 | 6 | 1 | 263.8 | 276.4 | 33 | 20 | 1 | 85.5 | 68.7 | |
| 19 | 2 | 1 | 165.4 | 177.5 | 21 | 4 | 1 | 141.3 | 137.3 | 23 | 10 | 1 | 137.5 | 100.1 | 27 | 10 | 1 | 159.3 | 104.5 | 34 | 2 | 1 | 190.5 | 213.7 | |
| 19 | 4 | 1 | 82.3 | 82.0 | 21 | 7 | 1 | 162.6 | 157.0 | 23 | 18 | 1 | 180.8 | 185.5 | 27 | 13 | 1 | 124.5 | 106.9 | 34 | 12 | 1 | 101.5 | 119.3 | |
| 19 | 5 | 1 | 145.6 | 144.3 | 21 | 8 | 1 | 140.9 | 111.4 | 23 | 24 | 1 | 116.0 | 133.0 | 28 | 1 | 1 | 151.5 | 145.0 | 35 | 7 | 1 | 150.2 | 164.3 | |
| 19 | 7 | 1 | 153.6 | 134.9 | 21 | 10 | 1 | 132.7 | 103.6 | 23 | 26 | 1 | 72.9 | 82.6 | 28 | 2 | 1 | 166.6 | 169.5 | 35 | 19 | 1 | 31.5 | 22.2 | |
| 19 | 9 | 1 | 112.5 | 99.7 | 21 | 11 | 1 | 166.8 | 154.0 | 24 | 1 | 1 | 151.7 | 174.3 | 28 | 8 | 1 | 203.5 | 193.2 | 36 | 5 | 1 | 133.7 | 140.7 | |
| 19 | 10 | 1 | 141.8 | 122.8 | 21 | 12 | 1 | 155.9 | 151.4 | 24 | 9 | 1 | 181.3 | 175.1 | 28 | 12 | 1 | 142.3 | 125.0 | 37 | 1 | 1 | 100.6 | 42.1 | |
| 19 | 12 | 1 | 177.0 | 178.5 | 21 | 13 | 1 | 174.4 | 171.4 | 24 | 13 | 1 | 251.9 | 276.2 | 28 | 21 | 1 | 132.4 | 155.7 | 37 | 9 | 1 | 149.5 | 173.9 | |
| 19 | 15 | 1 | 125.0 | 102.9 | 21 | 14 | 1 | 125.8 | 109.9 | 24 | 19 | 1 | 124.6 | 126.4 | 28 | 24 | 1 | 63.2 | 39.6 | 38 | 3 | 1 | 119.7 | 109.8 | |
| 19 | 16 | 1 | 284.2 | 300.4 | 21 | 15 | 1 | 124.9 | 115.8 | 25 | 2 | 1 | 97.6 | 95.1 | 28 | 16 | 1 | 175.5 | 208.6 | 38 | 3 | 1 | 85.2 | 92.1 | |
| 19 | 18 | 1 | 150.7 | 92.4 | 21 | 28 | 1 | 88.9 | 94.1 | 25 | 4 | 1 | 159.2 | 147.1 | 30 | 4 | 1 | 170.2 | 179.9 | 39 | 1 | 1 | 95.4 | 104.9 | |
| 19 | 19 | 1 | 162.7 | 150.3 | 22 | 2 | 1 | 130.4 | 133.0 | 25 | 7 | 1 | 178.6 | 197.0 | 31 | 8 | 1 | 154.6 | 143.1 | 39 | 4 | 1 | 96.3 | 120.4 | |
| 20 | 2 | 1 | 99.2 | 101.1 | 22 | 3 | 1 | 186.0 | 185.7 | 25 | 11 | 1 | 159.6 | 144.8 | 31 | 9 | 1 | 168.5 | 153.4 | 39 | 5 | 1 | 105.7 | 92.5 | |
| 20 | 4 | 1 | 141.6 | 95.0 | 22 | 4 | 1 | 119.2 | 134.2 | 25 | 18 | 1 | 185.9 | 184.2 | 31 | 11 | 1 | 165.8 | 160.9 | 40 | 4 | 1 | 112.1 | 132.2 | |
| 20 | 5 | 1 | 236.9 | 245.0 | 22 | 5 | 1 | 92.6 | 98.5 | 25 | 19 | 1 | 108.1 | 109.5 | | | | | | | | | | | |
| 20 | 7 | 1 | 248.8 | 253.3 | 22 | 6 | 1 | 236.7 | 238.7 | | | | | | | | | | | | | | | | |

Table 5. Interatomic distances and standard deviations for Hf₂P (in Ångström units).

| Atoms | Dist. | St.dev. | Atoms | Dist. | St.dev. |
|--------------|-------|---------|--------------|-------|---------|
| Hf(1) — P(1) | 2.576 | 0.020 | Hf(2) — P(1) | 2.629 | 0.020 |
| — P(2) | 2.729 | 0.017 | — P(3) | 2.658 | 0.011 |
| — Hf(6) | 3.032 | 0.003 | — P(2) | 2.683 | 0.016 |
| — P(3) | 3.061 | 0.014 | — Hf(3) | 3.103 | 0.003 |
| — Hf(6) | 3.086 | 0.003 | — Hf(1) | 3.215 | 0.004 |
| — Hf(2) | 3.215 | 0.004 | — Hf(4) | 3.240 | 0.003 |
| — Hf(5) | 3.375 | 0.004 | — Hf(6) | 3.396 | 0.004 |
| — Hf(4) | 3.561 | 0.004 | — Hf(5) | 3.481 | 0.004 |
| — Hf(1) | 3.574 | 0.000 | — Hf(4) | 3.548 | 0.004 |
| — Hf(1) | 3.841 | 0.006 | — Hf(2) | 3.574 | 0.000 |
| Hf(3) — P(1) | 2.685 | 0.020 | Hf(4) — P(2) | 2.628 | 0.016 |
| — P(2) | 2.762 | 0.022 | — P(1) | 2.644 | 0.015 |
| — P(3) | 2.846 | 0.015 | — P(3) | 2.949 | 0.015 |
| — Hf(2) | 3.103 | 0.003 | — Hf(6) | 3.114 | 0.003 |
| — Hf(5) | 3.109 | 0.003 | — Hf(3) | 3.225 | 0.003 |
| — Hf(5) | 3.175 | 0.004 | — Hf(2) | 3.240 | 0.003 |
| — Hf(4) | 3.225 | 0.003 | — Hf(2) | 3.548 | 0.004 |
| — Hf(3) | 3.226 | 0.006 | — Hf(1) | 3.561 | 0.004 |
| — Hf(3) | 3.574 | 0.000 | — Hf(4) | 3.574 | 0.000 |
| — Hf(5) | 3.593 | 0.004 | — Hf(5) | 3.593 | 0.004 |
| Hf(5) — P(1) | 2.631 | 0.015 | Hf(6) — P(3) | 2.623 | 0.011 |
| — P(3) | 2.713 | 0.011 | — P(2) | 2.702 | 0.022 |
| — Hf(3) | 3.109 | 0.003 | — Hf(1) | 3.032 | 0.003 |
| — Hf(3) | 3.175 | 0.004 | — Hf(1) | 3.086 | 0.003 |
| — Hf(1) | 3.375 | 0.004 | — Hf(4) | 3.114 | 0.003 |
| — Hf(6) | 3.393 | 0.004 | — Hf(6) | 3.146 | 0.005 |
| — Hf(2) | 3.481 | 0.004 | — Hf(5) | 3.393 | 0.004 |
| — Hf(5) | 3.574 | 0.000 | — Hf(2) | 3.396 | 0.004 |
| — Hf(4) | 3.593 | 0.004 | — Hf(6) | 3.574 | 0.000 |
| — Hf(5) | 4.039 | 0.006 | | | |
| P(1) — Hf(1) | 2.576 | 0.020 | P(2) — Hf(4) | 2.628 | 0.016 |
| — Hf(2) | 2.629 | 0.020 | — Hf(2) | 2.683 | 0.016 |
| — Hf(5) | 2.631 | 0.015 | — Hf(6) | 2.702 | 0.022 |
| — Hf(4) | 2.644 | 0.015 | — Hf(1) | 2.729 | 0.017 |
| — Hf(3) | 2.685 | 0.020 | — Hf(3) | 2.762 | 0.022 |
| P(3) — Hf(6) | 2.623 | 0.011 | | | |
| — Hf(2) | 2.658 | 0.011 | | | |
| — Hf(5) | 2.713 | 0.011 | | | |
| — Hf(3) | 2.846 | 0.015 | | | |
| — Hf(4) | 2.949 | 0.015 | | | |
| — Hf(1) | 3.061 | 0.014 | | | |

DISCUSSION

The crystal structure of Ta_2P is thoroughly described as well as compared with the structures of some other Me_2P compounds in Ref. 1, where a figure of the structure is also presented. The bonding in the isotypic Ti_2S was recently interpreted in terms of atomic valencies of the Pauling type.²

The interatomic distances of Hf_2P , Ta_2P , and Ti_2S will now be examined in terms of the trigonal prismatic arrangement of metal atoms (denoted A atoms) about the non-metal atoms X. These atoms also coordinate one to three further metal atoms (denoted B atoms), situated outside the quadrilateral sides of the prism. This description was used in earlier reports.⁷⁻⁹

Table 6 presents the metal-nonmetal distances classified as either X—A or X—B distances. The X(1)-metal and X(2)-metal distances are close to the radius sum. In Ta_2P , however, one P(2)—Ta distance exceeds the radius sum by 0.15 Å. This increase in X—B distance as compared to the radius sum is even more pronounced in the X(3)—B distances of Ta_2P , where one distance exceeds the radius sum by 0.44 Å. A similar tendency towards 8-coordination was observed in Nb_3P but not in Zr_3P in an investigation by Nawapong.¹¹ This remote third B atom also affects the average distances as revealed in Table 7. Assuming uniform expansion of the prisms as the radius ratio increases and assuming direct contact between A and B atoms, the calculated and observed average distances of X—B type agree within 2 % for Ti_2S and Hf_2P , while those of Ta_2P disagree by 7 % (including the more remote third B neighbour of the P(3) atom). If this B atom is excluded (it corresponds to a Pauling bond number of less than 0.2), the observed average distance is 1.04 (expressed in fractions of the atomic radius sum) in perfect agreement with the calculated value. The assumption of an average A—B distance

Table 6. X—Me distances in Å for Ti_2S , Hf_2P and Ta_2P . Data for Ti_2S is taken from Ref. 2 and for Ta_2P from Ref. 1.

| Atoms | Distance type | Ti_2S | Hf_2P | Ta_2P | |
|-------|---------------|---------|---------|---------|------|
| X(1)— | Me(1) | A—X | 2.44 | 2.58 | 2.47 |
| | Me(2) | A—X | 2.44 | 2.63 | 2.44 |
| | Me(3) | B—X | 2.51 | 2.69 | 2.55 |
| | 2 Me(4) | A—X | 2.49 | 2.64 | 2.58 |
| | 2 Me(5) | A—X | 2.49 | 2.63 | 2.54 |
| X(2)— | 2 Me(1) | A—X | 2.53 | 2.73 | 2.57 |
| | 2 Me(2) | A—X | 2.49 | 2.68 | 2.53 |
| | Me(3) | B—X | 2.62 | 2.76 | 2.71 |
| | 2 Me(4) | A—X | 2.48 | 2.63 | 2.54 |
| | Me(6) | B—X | 2.52 | 2.70 | 2.64 |
| X(3)— | Me(1) | B—X | 2.71 | 3.06 | 2.72 |
| | 2 Me(2) | A—X | 2.48 | 2.66 | 2.53 |
| | Me(3) | B—X | 2.58 | 2.85 | 2.64 |
| | Me(4) | B—X | 2.85 | 2.95 | 3.00 |
| | 2 Me(5) | A—X | 2.53 | 2.71 | 2.59 |
| | 2 Me(6) | A—X | 2.44 | 2.62 | 2.49 |

Table 7. Average distances for the compounds Ti₂S, Hf₂P, and Ta₂P, expressed in fractions of the atomic radius sum. Radii used are the 12-coordinated metal radii,¹⁰ $r_P = 1.10$ Å and $r_S = 1.04$ Å. The calculated distances are 1.00 if not otherwise stated.

| Distance type | No. of indep. distances | Ti ₂ S | Hf ₂ P | Ta ₂ P |
|--------------------|-------------------------|-------------------|-------------------|-------------------|
| X(1)-A } -B } | 5 | 0.99 | 0.98 | 1.01 |
| X(2)-A } -B } | 5 | 1.02 | 1.01 | 1.02 |
| X(3)-A | 3 | 1.00 | 0.99 | 0.98 |
| X(3)-B | 3 | 1.09 | 1.10 | 1.11 |
| X(3)-B, calculated | | 1.08 | 1.11 | 1.04 |
| A-B | 9 | 1.01 | 1.00 | 1.02 |
| A-A | 10 | 1.11 | 1.09 | 1.13 |
| A-A, calculated | | 1.13 | 1.11 | 1.15 |

close to the radius sum is nicely verified (see Table 7). The calculated expansion of the prism is also in fair agreement with the observed average distance.

There are also further metal-metal interactions in the Ta₂P type structure. Of particular interest is perhaps the distorted body-centered cubic metal coordination about the Me(3) atom. The observed distances between the central atom in the cube and the corner atoms (3.10 Å, 3.23 Å, 3.11 Å and 3.18 Å in Hf₂P) are close to the radius sum, while the cube edges are 10–14 % larger with one exception. This is the very long Hf(5)-Hf(5) distance of 4.04 Å, which may be considered as the result of the central atoms of the two neighbouring cubes approaching each other as close as 3.23 Å. In a b.c.c. metal the corresponding distance is 3.58 Å, assuming hard spheres with $r = 1.55$ Å.

In discussing the Ta₂P type structure it is interesting to note the high degree of space filling, defined as the ratio of the volume of the atoms in the unit cell to the volume of the unit cell.^{10,12} A correlation between space filling and radius ratio for six different compounds is demonstrated in Fig. 1. The cell dimensions from a recent investigation by Franzen, Smeggil and Conard¹³ were used in this diagram. It is reasonable to assume that the high values of space filling result from the high coordination numbers of the metal atoms.

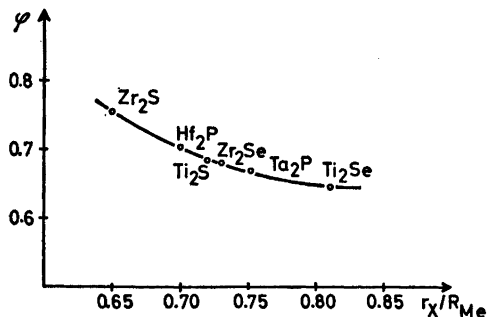


Fig. 1. Space filling function ϕ for six compounds¹³ with the Ta₂P type structure. Atomic radii according to Table 7 and with $r_{Sc} = 1.17$ Å.

From the discussion presented here it is evident that the Ta₂P type structure is largely in conformity with the size factor principle.

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