montré qu'elles étaient en accord avec les distances observées dans divers oxydes de vanadium et vanadates, les longueurs des liaisons V—O devraient être les suivantes:

	V^{III}	V^{IV}	V^{V}
V—O (Å)	2,02	1,97	1,92.

Or dans notre composé toutes les distances V—O sont inférieures à 1,89 Å.

Des mesures magnétiques effectuées sur des monocristaux montrent que $La_5V_3O_6S_7$ possède, entre 30 et 800 K, un comportement paramagnétique correspondant à un moment $\mu = 4{,}0\,\mu_B$ ($1\,\mu_B = 1$ Bohr magneton $\equiv 9{,}274 \times 10^{-24}$ JT^{-1}). Si cette valeur semble en faveur de la première possibilité (Tableau 3), les deux moments magnétiques calculés nous semblent trop proches pour que l'on puisse en tirer une conclusion. De plus si la présence dans un même composé de vanadium(III) et de vanadium(IV) est bien connue (tels les oxydes V_nO_{2n-1}), nous n'avons trouvé aucun dérivé décrit qui contienne à la fois V^{III} et V^{V}.

Ainsi la deuxième hypothèse qui donne deux états d'oxydation proches l'un de l'autre paraît-elle plus vraisemblable. Mais d'autres méthodes d'investigation sont nécessaires pour trancher ce point.

Nous tenons à remercier Monsieur le Professeur N. Rodier qui a bien voulu nous apporter son aimable collaboration lors des mesures expérimentales.

Tableau 3. *Valences possibles du vanadium et moments magnétiques correspondants*

Site	Multiplicité	1ère possibilité	2ème possibilité
V(1)	2	V^{V}	V^{III}
V(2)	4	V^{III}	V^{IV}
Moment magnétique calculé (μ_B)		4,04	3,74

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$Hf_2Ru_3Si_4$ and $Zr_2Ru_3Si_4$ with Infinite Si-Centered Square Antiprism Columns and Infinite Ru-Centered Octahedron Columns

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Abstract. $Hf_2Ru_3Si_4$: $M_r = 772{\cdot}5$, monoclinic, $mC72$, $C2/c$, $a = 18{\cdot}949\,(5)$, $b = 5{\cdot}3252\,(8)$, $c = 13{\cdot}227\,(5)$ Å, $\beta = 127{\cdot}61\,(2)°$, $V = 1057{\cdot}3\,(5)$ Å^3, $Z = 8$, $D_x = 9{\cdot}705$ g cm^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}71069$ Å, $\mu = 501$ cm^{-1}, $F(000) = 2656$, $T = 293$ K, $wR = 0{\cdot}053$ for 2915 contributing independent reflections. $Zr_2Ru_3Si_4$ is isotypic: $M_r = 597{\cdot}99$, $a = 18{\cdot}992\,(3)$, $b = 5{\cdot}3476\,(8)$, $c = 13{\cdot}289\,(3)$ Å, $\beta = 127{\cdot}73\,(1)°$, $V = 1067{\cdot}4\,(4)$ Å^3, $D_x = 7{\cdot}441$ g cm^{-3}, $\lambda(\text{Mo }K\alpha)$, $\mu = 127$ cm^{-1}, $F(000) = 2144$, $T = 293$ K, $R = 0{\cdot}056$ for 1444 contributing independent reflections. The structure is characterized by infinite columns of face-joined

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square antiprisms and infinite isolated columns of face-joined octahedra. Each antiprism is formed by 4 Hf(Zr) and 4 Ru atoms and is centered by an Si atom. The octahedra are formed by Si atoms and are centered by Ru atoms. $Hf_2Ru_3Si_4$ is a site-exchange variant of the $Sc_3Re_2Si_4$ type in which each antiprism consists of 6 Sc and 2 Re atoms.

Introduction. Ternary silicides $R_xT_ySi_z$ containing a rare-earth element (R) and a transition element (T) are extensively studied for their superconducting properties. Eleven structure types of superconducting ternary silicides have been listed in a recent review (Braun, 1984), of which two have not yet been determined. Recently, superconductivity has been found in two ternary silicides belonging to two additional structure types: $Y_2Mo_3Si_4$ (Aliev, Gorelenko, Moshchalkov & Skolozdra, 1983) with $U_2Mo_3Si_4$ type (Sikiritsa, Akselrud & Yarmolyuk, 1978) and $Zr_2Ru_3Si_4$ (Braun, 1985). The powder X-ray diffraction pattern of $Zr_2Ru_3Si_4$ could not be matched with any of the three structure types known at this composition among the ternary intermetallic silicides:

–$Sc_2Re_3Si_4$ ($tP36$, $P4_12_12$) type (Pecharskii, Bodak & Gladyshevskii, 1978), a ternary ordered Zr_5Si_4-type derivative;

–$Ce_2Sc_3Si_4$ ($oP36$, $Pnma$) type (Mokraya, Bodak & Gladyshevskii, 1979), a ternary ordered Sm_5Ge_4-type derivative;*

–the above-mentioned $U_2Mo_3Si_4$ ($mP18$, $P2_1/c$) type, a structure related to the two preceding ones.

In this paper we report on the new $Zr_2Ru_3Si_4$ structure and on its prototype, $Hf_2Ru_3Si_4$.

Experimental. Compounds of nominal compositions $Zr_{20}Ru_{35}Si_{45}$ and $Hf_2Ru_3Si_4$ were prepared by arc melting under argon from Zr(99·9%),† Hf(99·98%),† Ru(99·9%)† and Si(99·999%). The purity given for Hf accounts only for impurities other than Zr. According to the batch analysis furnished by the supplier (Material Research Corp.) the Hf starting material contains 3 wt% Zr. Thus, the Hf sample actually had the nominal composition $(Hf_{0.943}Zr_{0.057})_2Ru_3Si_4$. The samples were annealed at 1270 K in quartz tubes under argon for one week. The $Hf_2Ru_3Si_4$ sample was remelted and allowed to cool slowly using a levitation technique to favor crystal growth. Single crystals of irregular shape with 60 and 50 μm mean diameter for Zr and Hf samples were obtained from crushed ingots. Automatic four-circle diffractometer (Philips PW 1100). Laue symmetry $2/m$. Lattice parameters given in the *Abstract* from average θ values of reflections and antireflections: 19 for $Hf_2Ru_3Si_4$ (nine in the range $17° < 2\theta < 21°$, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å; ten with $35° < 2\theta < 61°$, Mo $K\alpha_1$, $\lambda = 0{\cdot}70930$ Å) and 17 for $Zr_2Ru_3Si_4$ (six with $17° < 2\theta < 19°$, Mo $K\alpha$; eleven with $28° < 2\theta < 49°$, Mo $K\alpha_1$). Data collection for $Hf_2Ru_3Si_4$ ($Zr_2Ru_3Si_4$): $\sin\theta/\lambda < 0{\cdot}91$ ($0{\cdot}71$) Å^{-1}; spherical-absorption correction: 4·63 (1·77) < s.a.c. < 5·71 (1·80); 3254 (1555) unique reflections measured; h and k positive up to 34 (26) and 9 (7) and -23 $(-18) \leq l \leq 18$ (14); ω–2θ scan; ω-scan angle $[1{\cdot}1\ (1{\cdot}0) + 0{\cdot}1\tan\theta]°$; 2915 (1444) contributing reflections of which 2238 (1235) with $|F| > 3\sigma(F)$ and 677 (209) less-than calc. > obs.; systematic absences hkl: $h+k \neq 2n$, $h0l$: $l \neq 2n$, $h \neq 2n$, $0k0$: $k \neq 2n$. $Zr_2Ru_3Si_4$ structure solved using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) in space group $C2/c$. $Hf_2Ru_3Si_4$ was recognized as being isotypic using the *LAZY PULVERIX* program (Yvon, Jeitschko & Parthé, 1977) and confirmed by refinement of single-crystal data. We prefer to call this structure type $Hf_2Ru_3Si_4$. Since Hf and Ru have 28 electrons difference instead of 4 for Zr and Ru, the atom distribution can be determined with less ambiguity in the Hf compound. $Hf_2Ru_3Si_4$ ($Zr_2Ru_3Si_4$) was refined by full-matrix least squares using F values. 38 (38) parameters refined: 1 (1) scale factor, 1 (1) secondary isotropic extinction parameter, 36 (36) positional and isotropic thermal parameters. $R = 0{\cdot}072$ ($0{\cdot}056$), $wR = 0{\cdot}053$ ($0{\cdot}059$), $S = 1{\cdot}40$ ($2{\cdot}17$); $w = 1/\sigma^2(F)$ for $Hf_2Ru_3Si_4$ and, for $Zr_2Ru_3Si_4$, $w = \exp[15(\sin\theta/\lambda)^2]/\sigma^2(F)$ as proposed by Dunitz & Seiler (1973); final $(\Delta/\sigma)_{max} = 4 \times 10^{-4}$ (5×10^{-4}); final residual electron density $[-9{\cdot}7\ (-3{\cdot}8) <$ r.e.d. $< 17{\cdot}5\ (5{\cdot}2)]$ e Å^{-3}; secondary extinction of type 1 with a Gaussian distribution (Becker & Coppens, 1974*a*,*b*) of $13{\cdot}19\,(1) \times 10^{-6}$ $[12{\cdot}12\,(3) \times 10^{-6}]$; atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974); all programs used for structure refinement from the *XRAY*76 system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Atomic and thermal parameters are given in Table 1, interatomic distances for $Hf_2Ru_3Si_4$ in Table 2. The interatomic distances for $Zr_2Ru_3Si_4$ have been deposited.*

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* Another recently reported ternary derivative of Sm_5Ge_4 is $Zr_2Nb_3Ge_4$ (Seropegin, Tabachenko & Mys'kiv, 1984). $Zr_2Nb_3Ge_4$ and $Ce_2Sc_3Si_4$ (same space group, same relative lattice dimensions and same number of atoms in the unit cell as for Sm_5Ge_4) differ only in the atom occupation of the two sites with Wyckoff notation 8(d) where Zr replaces Sc and Nb replaces Ce while in the metal position 4(c) Sc is replaced by Nb. The composition remains unchanged ($Ce_8Sc_8Sc_4Si_{16}$ and $Nb_8Zr_8Nb_4Ge_{16}$). The atom ordering proposed for $Zr_2Nb_3Ge_4$ is, however, difficult to verify since between Zr and Nb there is only one electron difference.

† Non-metallic impurities not included.

* Lists of structure factors for both compounds arranged in a standard crystallographic data file (Brown, 1983) and the interatomic distances for $Zr_2Ru_3Si_4$ have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42178 (43 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atom positions for* $Hf_2Ru_3Si_4$ *and* $Zr_2Ru_3Si_4$, *space group C2/c*

The isotropic temperature factors are expressed as: $T = \exp[-2\pi^2 U(2\sin\theta/\lambda)^2]$. Estimated standard deviations are given in parentheses.

		x	*y*	*z*	*U*×100(Å²)
$Hf_2Ru_3Si_4$					
Ru(1)	8(*f*)	0·02046 (8)	0·1160 (3)	0·4161 (1)	0·76 (2)
Si(1)	8(*f*)	0·1136 (3)	0·1425 (9)	0·1063 (4)	0·61 (6)
Hf(1)	8(*f*)	0·16568 (4)	0·1300 (2)	0·36130 (6)	0·73 (1)
Ru(2)	8(*f*)	0·23780 (7)	0·4107 (3)	0·2192 (1)	0·47 (2)
Si(2)	8(*f*)	0·2655 (3)	0·1230 (9)	0·1046 (4)	0·61 (6)
Si(3)	8(*f*)	0·3292 (3)	0·2413 (9)	0·4363 (4)	0·64 (7)
Ru(3)	8(*f*)	0·37790 (8)	0·1449 (3)	0·0687 (1)	0·82 (2)
Hf(2)	8(*f*)	0·42668 (4)	0·1301 (1)	0·35194 (6)	0·73 (1)
Si(4)	4(*e*)	0	0·3816 (13)	¼	0·68 (9)
Si(5)	4(*e*)	0	0·8772 (12)	¼	0·51 (9)
$Zr_2Ru_3Si_4$					
Ru(1)	8(*f*)	0·02120 (7)	0·1116 (2)	0·41563 (10)	0·47 (3)
Si(1)	8(*f*)	0·1128 (3)	0·1426 (7)	0·1058 (3)	0·54 (6)
Zr(1)	8(*f*)	0·16601 (9)	0·1277 (2)	0·3618 (1)	0·47 (3)
Ru(2)	8(*f*)	0·23791 (7)	0·4087 (2)	0·2200 (1)	0·34 (3)
Si(2)	8(*f*)	0·2657 (3)	0·1227 (8)	0·1047 (4)	0·61 (6)
Si(3)	8(*f*)	0·3298 (3)	0·2432 (7)	0·4353 (4)	0·29 (6)
Ru(3)	8(*f*)	0·37707 (7)	0·1411 (3)	0·0664 (1)	0·61 (3)
Zr(2)	8(*f*)	0·42666 (9)	0·1290 (3)	0·3522 (2)	0·52 (4)
Si(4)	4(*e*)	0	0·3823 (11)	¼	0·60 (9)
Si(5)	4(*e*)	0	0·8717 (11)	¼	0·41 (8)

The atom positions given in Table 1 for $Hf_2Ru_3Si_4$ correspond to a refinement which assumes that the single crystal studied was free of Zr impurities. The presence of Zr in the batch analysis supplied for Hf leads us, however, to check for a possible mixed occupation of Hf and Zr atoms on the two Hf sites. Refinement of the population was carried out on Hf, assuming a total occupancy equal to unity and constraining the temperature factors of Zr atoms to equal those of Hf. The resulting *wR* value was 0·051 (instead of 0·053) and the population for Zr was found to be relatively high: 0·100 (8) and 0·068 (8) on the Hf(1) and Hf(2) sites respectively. The structure refinement, however, did not significantly change the fractional positional coordinates of the atoms (maximum change smaller than 1×10^{-4}).

Discussion. A drawing of $Hf_2Ru_3Si_4$ is shown in Fig. 1. The structure is a site-exchange variant of the $Sc_3Re_2Si_4$ structure and can be classified with the family of structures characterized by infinite columns of face-shared Si-centered square antiprisms and infinite columns of face-shared transition-metal-centered Si octahedra (Chabot & Parthé, 1985). In neither of these structures are the octahedron columns edge-shared with other octahedron columns. The antiprism and octahedron columns are arranged along [100] in two structural slabs, parallel to the (001) plane, one represented by empty circles and the other by circles with inscribed crosses. The two kinds of slabs are related by a *c* glide plane perpendicular to the *b* axis. It is interesting to mention that two such structural slabs, with the same composition as in $Hf_2Ru_3Si_4$, are also present in the $ScRe_2Si_3$ structure type (see Fig. 6*b* in Pecharskii, Bodak & Gladyshevskii, 1979). In this structure, however, they are not related by a *c* glide plane and, furthermore, there is an additional plane of Re and Si atoms between the slabs.

Table 2. *Interatomic distances d (less than* 3·5 Å) *and rounded values* $\Delta \equiv [100(d-\sum r)/\sum r]$ (%) *for* $Hf_2Ru_3Si_4$

E.s.d.'s are given in parentheses. The atomic radii *r* used for Hf, Ru and Si are 1·580, 1·339 and 1·319 Å respectively (Teatum, Gschneidner & Waber, 1960).

	d (Å)	*Δ*(%)		*d* (Å)	*Δ*(%)
Hf(1)—1Si(3)	2·680 (6)	−7·6	Hf(2)—1Si(3)	2·743 (7)	−5·3
1Si(3)	2·707 (6)	−6·7	1Si(5)	2·787 (4)	−3·9
1Si(2)	2·843 (5)	−1·9	1Si(4)	2·790 (3)	−3·8
1Si(4)	2·859 (3)	−1·4	1Si(2)	2·800 (4)	−3·4
1Si(5)	2·863 (4)	−1·2	1Si(1)	2·854 (7)	−1·5
1Ru(2)	2·867 (2)	−1·8	1Ru(2)	2·896 (2)	−0·8
1Si(1)	2·879 (6)	−0·7	1Ru(1)	2·914 (2)	−0·1
1Si(2)	2·884 (4)	−0·5	1Ru(1)	2·955 (2)	+1·2
1Si(2)	2·911 (5)	+0·4	1Si(1)	2·974 (5)	+2·5
1Ru(3)	3·024 (2)	+3·6	1Ru(1)	3·088 (2)	+5·8
1Ru(3)	3·161 (2)	+8·3	1Ru(3)	3·175 (3)	+8·7
1Ru(1)	3·180 (2)	+8·9	1Ru(2)	3·233 (2)	+10·8
1Ru(1)	3·246 (2)	+11·2	1Ru(3)	3·266 (2)	+11·9
1Ru(2)	3·282 (2)	+12·4	1Si(1)	3·284 (4)	+13·3
1Hf(1)	3·316 (1)	+4·9	1Hf(2)	3·420 (2)	+8·2
1Hf(2)	3·475 (1)	+10·0	1Hf(1)	3·475 (1)	+10·0
1Hf(2)	3·477 (2)	+10·0	1Hf(1)	3·477 (2)	+10·0
Ru(1)—1Si(5)	2·357 (4)	−11·3	Ru(2)—1Si(1)†	2·350 (5)	−11·6
1Si(1)	2·374 (6)	−10·7	1Si(3)†	2·399 (5)	−9·7
1Si(3)	2·391 (4)	−10·0	1Si(2)†	2·426 (6)	−8·7
1Si(1)	2·433 (4)	−8·5	1Si(3)†	2·447 (5)	−7·9
1Si(4)	2·437 (4)	−8·3	1Si(1)†	2·617 (4)	−1·6
1Hf(2)	2·914 (2)	−0·1	1Si(2)†	2·625 (6)	−1·3
1Hf(2)	2·955 (2)	+1·2	2Ru(2)	2·740 (2)	+2·3
1Ru(1)	3·025 (3)	+13·0	1Hf(1)	2·867 (2)	−1·8
1Hf(2)	3·088 (2)	+5·8	1Hf(2)	2·896 (2)	−0·8
1Ru(3)	3·094 (2)	+15·5	1Ru(3)	3·034 (2)	+13·3
1Hf(1)	3·180 (2)	+8·9	1Hf(2)	3·233 (2)	+10·8
1Hf(1)	3·246 (2)	+11·2	1Hf(1)	3·282 (2)	+12·4
1Ru(3)	3·348 (2)	+25·0			
Ru(3)—1Si(5)	2·421 (4)	−8·9	Si(1)—1Ru(2)	2·350 (5)	−11·6
1Si(2)	2·452 (6)	−7·7	1Ru(1)	2·374 (6)	−10·7
1Si(3)	2·485 (5)	−6·5	1Ru(1)	2·433 (4)	−8·5
1Si(4)	2·510 (4)	−5·6	1Si(3)	2·609 (8)	−1·1
1Si(2)	2·561 (4)	−3·6	1Ru(2)	2·617 (4)	−1·6
1Si(1)	2·670 (6)	+0·5	1Ru(3)	2·670 (6)	+0·5
1Hf(1)	3·024 (2)	+3·6	1Hf(2)	2·854 (7)	−1·5
1Ru(2)	3·034 (2)	+13·3	1Hf(1)	2·879 (6)	−0·7
1Ru(1)	3·094 (2)	+15·5	1Si(2)	2·894 (8)	+9·7
1Hf(1)	3·161 (2)	+8·3	1Hf(2)	2·974 (5)	+2·5
1Hf(2)	3·175 (3)	+8·7	1Hf(2)	3·284 (4)	+13·3
1Hf(2)	3·266 (2)	+11·9			
1Ru(1)	3·348 (2)	+25·0			
Si(2)—1Ru(2)	2·426 (6)	−8·7	Si(3)—1Ru(1)	2·391 (4)	−10·0
1Ru(3)	2·452 (6)	−7·7	1Ru(2)	2·399 (5)	−9·7
1Si(3)	2·541 (7)	−3·7	1Ru(2)	2·447 (5)	−7·9
1Ru(3)	2·561 (4)	−3·6	1Ru(3)	2·485 (5)	−6·5
1Ru(2)	2·625 (6)	−1·3	1Si(2)	2·541 (7)	−3·7
1Hf(2)	2·800 (4)	−3·4	1Si(1)	2·609 (8)	−1·1
1Si(2)	2·802 (7)	+6·3	1Hf(1)	2·680 (6)	−7·6
1Hf(1)	2·843 (5)	−1·9	1Hf(1)	2·707 (6)	−6·7
1Hf(1)	2·884 (4)	−0·5	1Hf(2)	2·743 (7)	−5·3
1Si(1)	2·894 (8)	+9·7	1Si(4)	3·425 (5)	+29·8
1Hf(1)	2·911 (5)	+0·4			
Si(4)—2Ru(1)*	2·437 (4)	−8·3	Si(5)—2Ru(1)*	2·357 (4)	−11·3
2Ru(3)*	2·510 (4)	−5·6	2Ru(3)*	2·421 (4)	−8·9
1Si(5)	2·639 (10)	0·0	1Si(4)	2·639 (10)	0·0
1Si(5)	2·686 (10)	+1·8	1Si(4)	2·686 (10)	+1·8
2Hf(2)*	2·790 (3)	−3·8	2Hf(2)*	2·787 (4)	−3·8
2Hf(1)*	2·859 (3)	−1·4	2Hf(1)*	2·863 (4)	−1·2
2Si(3)	3·425 (5)	+29·8			

* Antiprism.
† Octahedron.

As can be seen in Table 2, the limits of the coordination polyhedra of the Si atoms are always well defined in $Hf_2Ru_3Si_4$. The geometry of the polyhedra, however, is well characterized only for the square antiprisms forming columns and which are alternately centered by Si(4) or Si(5) atoms arranged along a string parallel to [010]. In $Hf_2Ru_3Si_4$, the vertices of the slightly deformed antiprisms are occupied by 4 Hf and 4 Ru atoms which are distributed on two tetrahedra rotated by 90° around the column axis. In the $Sc_3Re_2Si_4$ site-exchange variant (Fig. 3 in Chabot & Parthé, 1985) the antiprisms are formed by 6 Sc and 2 Re atoms. This constitutes the essential difference between these two structure types. For both compounds, it does not seem possible to change the antiprism composition. Neither a $Hf_3Ru_2Si_4$ with $Sc_3Re_2Si_4$ type nor a $Sc_2Re_3Si_4$ with $Hf_2Ru_3Si_4$ type could be synthesized using the above-described preparation methods. The already mentioned $Sc_2Re_3Si_4$ phase crystallizes in its own structure type which does not contain infinite columns of Si-centered antiprisms.

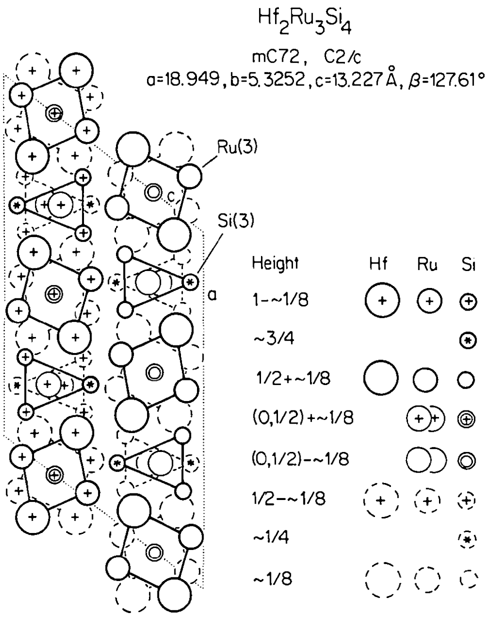

Fig. 1. The $Hf_2Ru_3Si_4$ structure type in a projection along the short *b* axis. Infinite square antiprism columns and infinite octahedron columns parallel to [010] are indicated.

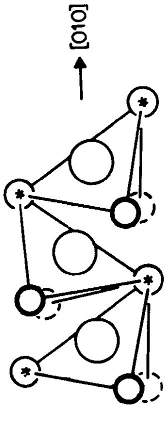

Fig. 2. Si-atom surrounding of the Ru(2) atoms forming chains in $Hf_2Ru_3Si_4$. The Si atoms are arranged in face-shared octahedron columns. The Ru atoms do not exactly center the octahedra but rather tend to be tetrahedrally surrounded by Si atoms as indicated on the drawing.

The limits of the coordination polyhedra for the Ru atoms are not so well defined as for the Si atoms. All the Ru coordination polyhedra contain Si atoms at short distances: Ru(1) is surrounded by a deformed square pyramid of 5 Si and, Ru(2) and Ru(3), by 6 Si atoms. The transition metal (*T*) centered Si octahedra forming columns in $Hf_2Ru_3Si_4$ and $Sc_2Re_3Si_4$ [$T = \mathrm{Ru}(2)$ and $T = \mathrm{Re}(2)$ respectively] are deformed in the same way. In particular, Si(3) deviates from the expected position which would allow the shared triangular Si faces to be parallel. As a consequence, the transition elements at the centers of the face-shared octahedra form a zigzag chain parallel to the column axis. One can note from Table 2 that the only Ru—Ru intermetallic distances are found along this chain. Furthermore, Ru(2) is not exactly located at the center of the Si octahedron but tends to be surrounded by a tetrahedron of 4 Si atoms (see Fig. 2), the $Ru(2)Si_4$ tetrahedra sharing vertices along [010].

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Structure of Cadmium Tellurate(IV), $CdTeO_3$

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Abstract. M_r = 288·0, monoclinic, $P2_1/c$, a = 7·790 (1), b = 11·253 (2), c = 7·418 (1) Å, β = 113·5 (1)°, V = 596·5 Å^3, Z = 8, D_m = 6·41 (1), D_x = 6·41 g cm^{-3}, λ(Ag $K\alpha$) = 0·56083 Å, μ = 80·3 cm^{-1}, $F(000)$ = 992, room temperature; final R = 0·034 for 3231 independent observed reflections. The structure consists of isolated slightly distorted trigonal TeO_3 pyramids (mean Te—O distance 1·89 Å) which are connected by Cd atoms; the resulting Cd—O coordination polyhedra are a trigonal prism [Cd—O 2·197 (6)–2·476 (6) Å] and an octahedron [Cd—O 2·284 (6)–2·365 (6) Å] both being rather distorted.

Introduction. Many tellurites of the type MTeO$_3$ (M: alkaline earths, Ni, Zn, Cd, Hg, Pb, *etc.*) have been extensively studied because of their promising nonlinear optical properties (Bergman, Boyd & Ashkin, 1969). Contrary to tellurites with small metal ions (Hanke, 1967; Kohn, Inoue, Horie & Akimoto, 1976) or large ones like Sr^{2+}, Ba^{2+}, Pb^{2+} (Burckhardt, Koçak, Külcü & Trömel, 1984; Folger, 1975; Young, 1979), there is a lack of knowledge concerning the structure of tellurites with medium-sized ions like Cd^{2+} (Hanke, 1983). Some other reasons for a structure determination of $CdTeO_3$ and $HgTeO_3$ were given in a previous paper (Brandt & Moritz, 1985) where both compounds were regarded as constituents of native oxide films on (Cd,Hg)Te semiconductor material; moreover, structural details are needed for the interpretation of their XPS spectra (Seelmann-Eggebert, Brandt & Richter, 1984).

Markovskii & Pron (1968) first prepared $CdTeO_3$ by precipitation and reported a cubic structure as well as a hexagonal modification above 770 K. Robertson, Shaw & Young (1978), when studying the system CdO–TeO_2, did not find the cubic phase, but two monoclinic phases with an irreversible phase transition from α- into β-$CdTeO_3$ at about 973 K. Comparison of the d values indicates that the α-phase of Robertson *et al.* (1978) is probably identical to the 'hexagonal' phase of Markovskii & Pron (1968). In addition, Wrobsewska, Erb, Dobrowolski & Freundlich (1979) gave lattice parameters of two $CdTeO_3$ modifications quite different from those of the former investigators.

In order to obtain an insight into the polymorphism of $CdTeO_3$, preliminary annealing and quenching experiments as well as DTA studies of mixtures of CdO and TeO_2 near the 1:1 composition were performed which confirmed the melting point of $CdTeO_3$ at 1068 K, but no indications of a phase transition between room and melting temperature could be encountered. SHG measurements showed no positive signals which is in accordance with the given space group. The lattice parameters correspond roughly to those of the β-phase of Robertson *et al.* (1978).

In this paper we present the structure of $CdTeO_3$; the structure of $HgTeO_3$ will be reported later.

Experimental. From a colourless Czochralski-grown crystal a single crystalline fragment (100 × 200 × 500 μm) was obtained. Automatic four-circle diffractometer (Enraf–Nonius CAD-4), graphite-mono-

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