Gd,Tb,Dy,Ho,Er,Yb,Y) and $Ln_2V_{10}O_{28}.24H_2O$ (Ln=Er,Yb,Tm,Lu,Y). Differences between them seem to be due to differences in the number of water molecules of crystallization rather than to changes in the ionic radius. In particular, the different number of water molecules of hydration seems to be responsible for cell distortion and the near doubling of one cell parameter in going from the 25-hydrate to the 24-hydrate. In the second case, decavanadate anions belonging to consecutive layers become crystallographically nonequivalent.

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Zr₃Ir with Tetragonal α-V₃S Structure

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Abstract. $M_r = 465.86$, *tI*32, *I*4̄2*m*, $a = 10.788$ (2), $c = 5.662$ (1) Å, $V = 658.9$ (2) Å³, $Z = 8$, $D_x = 9.39$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 51.3$ mm⁻¹, $F(000) = 1576$, $T = 293$ K, $R = 0.060$ for 490 independent reflections. Zr₃Ir is isotypic to α-V₃S belonging to a structure family comprising the structure types α- and β-V₃S, Ni₃P (Fe₃P), Ti₃P and Hf₃As. It is the first known example of a phase crystallizing with one of these structure types where both constituents are transition elements.

Introduction. There has been much interest in alloys of Zr with elements of the Fe, Co and Ni groups since many of these compounds are superconductors; Zr₂Rh with CuAl₂ type, for example, has a T_c of 11·3 K (McCarthy, 1971). The Zr–Ir phase diagram was studied by Kuprina & Kuruyachaya (1974) who confirmed the existence of binary compounds at five different compositions. ZrIr₃ crystallizes with the Cu₃Au structure type (Dwight & Bech, 1959) and ZrIr₂ with the cubic Laves type MgCu₂ (Dwight, 1961). At the equiatomic composition there are two structural variants; the high-temperature variant is known to crystallize with the CsCl-type structure (Eremenko, Semenova, Shtepa & Kudrjavtsev, 1978). At the Zr-rich side of the phase diagram only two phases were confirmed, namely Zr₂Ir with CuAl₂-type structure (McCarthy, 1971) and a phase at composition Zr₃Ir.

For these two compositions McCarthy (1971) measured superconducting transition temperatures of 7·33 and 2·13 K respectively. The earlier reported Zr_5Ir_3 with Mn_5Si_3 type (Biswas & Schubert, 1967) was not observed by Kuprina & Kuruyachaya (1974). Raman & Schubert (1964) measured the lattice parameters of a tetragonal phase with composition Zr_3Ir and identified it as being isotypic with β-U. However, this is doubtful because Zr_3Ir forms an exception to the valence electron concentration rule established for the σ phases (see, for example, Villars, Girgis & Hulliger, 1982). Dr R. M. Waterstrat, who had earlier studied the structure relationship affecting the stability of A15- and Ti_3P-type compounds with the same or similar stoichiometry (Waterstrat, 1981), decided to synthesize the Zr_3Ir phase in order to establish its crystal structure.

In the course of our structural studies of compounds formed by Sc, Zr and Hf with elements of the Fe, Co or Ni groups belonging to the second and third long periods we have previously identified two structure types having ideal compositions close to 3:1. $Zr_{11}Os_4$, for example, crystallizes with the $Sc_{11}Ir_4$ structure type, $cF120$ (Chabot, Cenzual & Parthé, 1980), while in the Hf–Os system one finds a still more complicated structure at a similar composition, $Hf_{54}Os_{17}$, $oI142$ (Cenzual, Chabot & Parthé, 1985). It was of interest to see whether the structure of Zr_3Ir could be related to the two structure types observed with Os compounds.

Experimental. A sample was kindly provided by Dr R. M. Waterstrat who had first prepared the pure eutectic $(Zr + Zr_3Ir)$ at 18% Ir. The sample was then placed in a container of pure Ir and heated to 1433 K where the eutectic alloy melted. It was further maintained at 1443 K for 3 h in order to allow the diffusion of Ir from the container. The cell parameters given in the *Abstract* were refined from the 2θ values of 19 reflections $(17° \leq 2\theta \leq 62°)$ using the program *FINAX* (Hovestreydt, 1983). They are close to the parameters reported by Raman & Schubert (1964). Powder diffraction: Guinier Nonius camera, graphite-monochromated Cu $K\alpha$ radiation $(\lambda = 1·5418 \text{ Å})$, internal Si standard $(a = 5·4307 \text{ Å})$. The isotypy with the α-V_3S structure (Pedersen & Grønvold, 1959), or possibly the closely related Ni_3P structure (Aronsson, 1955), was recognized by comparison with the simulated powder diagram calculated using the program *LAZY PULVERIX* (Yvon, Jeitschko & Parthé, 1977). Single crystal of irregular shape (mean radius 21 μm); automatic four-circle diffractometer (Philips PW 1100); ω–2θ scan mode; graphite-monochromated Mo $K\alpha$ radiation. Laue symmetry $4/mmm$; systematic absences $h + k + l = 2n + 1$. 612 reflections collected out to $\sin\theta/\lambda = 0·7024 \text{ Å}^{-1}$ $(0 \leq h \leq 15, 0 \leq k \leq 10, k \leq h; 0 \leq l \leq 7$ and all antireflections), yielding 515 independent reflections assuming a noncentro-

Table 1. *Atomic coordinates and isotropic thermal parameters for* Zr_3Ir *with space group* $I\bar{4}2m$

The temperature factor is expressed as $T = \exp[-2\pi^2 U(2\sin\theta/\lambda)^2]$. E.s.d.'s are given in parentheses.

	x	y	z	$100U(\text{Å}^2)$
Zr(1) in 8(i)	0·0952 (3)	x	0·2610 (9)	0·98 (8)
Zr(2) in 8(i)	0·2940 (2)	x	0·2536 (8)	0·90 (7)
Zr(3) in 8(g)	0·3544 (3)	0	$\frac{1}{4}$	0·91 (7)
Ir(1) in 8(f)	0·2919 (1)	0	0	0·79 (4)

symmetric space group ($R_{int} = 0·039$), of which 451 were considered significant $[|I| \geq 3\sigma(I)]$. Standard reflections 552 and $55\bar{2}$ (max. intensity variation ±2·9%); spherical absorption correction ($\mu R = 1·077$; $4·140 \leq A^* \leq 4·556$). Full-matrix refinement from positions of Pb_3Au (Wang & Giessen, 1971), space group $I\bar{4}2m$, using F values of 490 independent reflections (including 39 less-thans calculated greater than observed). 6 positional parameters and 4 isotropic temperature factors, listed in Table 1, were refined to a final $R = 0·060$; isotropic secondary extinction [mosaic spread, Gaussian distribution, $G = 1·5 (2) \times 10^{-5}$]; absolute-structure parameter, $x = 0·06 (7)$ (Flack, 1983); $S = 7·59$; shift/error in the last cycle $\leq 0·0002$; max. (min.) height of final residual electron density map 5·9 $(-8·0) \text{ e Å}^{-3}$.† Atomic scattering factors for neutral atoms, f' and f'', from *International Tables for X-ray Crystallography* (1974); programs used for data reduction and structure refinement from the *XRAY76* system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

In order to be able to exclude definitely the closely related Ni_3P structure type, space group $I\bar{4}$, a refinement was also carried out on F values from reflections collected in $\frac{1}{8}$ of a sphere of reciprocal space. Although the positions of the Ni_3P structure were used as starting values the refinement converged rapidly to the positions of the α-V_3S type, space group $I\bar{4}2m$.

Discussion. The close geometrical relationship between the α-V_3S type and the β-V_3S (Pedersen & Grønvold, 1959), Ni_3P (Fe_3P) and Ti_3P (Lundström & Snell, 1967) structure types, all having tetragonal cells of similar dimensions, has been discussed in several publications (see Andersson, 1978; Rundqvist, Andersson & Pramatus, 1979; Wang & Giessen, 1971). A fifth structure, Hf_3As (Willerström, Carlsson & Rundqvist, 1980), with a larger, monoclinic cell, was later added to this structure family. These five structures, together with a hypothetical structure related to Hf_3As, are shown in a schematical presentation in Fig. 1. As

common features all these structures contain two kinds of columns of intergrown tetrahedron stars (a tetrahedron whose faces are capped by an extra atom) parallel to the fourfold axis (or pseudo fourfold axis in the case of Hf$_3$As and its related, hypothetical structure). In the first kind of column, drawn with dashed lines, the tetrahedron stars are formed exclusively by majority atoms while in the second kind of columns, drawn with heavy lines, the faces of the inner tetrahedra are capped by minority atoms. The tetrahedron star centers of the latter kind of columns (heavy lines) are shifted by $\frac{1}{4}$ along the short cell axis (perpendicular to the plane of projection) with respect to the other kind of columns. In the three structures on the left of Fig. 1 the two kinds of columns are oriented so that their respective tetrahedron stars form an angle of exactly 45° between them. These three structures differ in the orientation of the mixed tetrahedron star columns (heavy lines), some being rotated by 90° with respect to the corresponding columns in the other structures. The three structures on the right in Fig. 1 are all analogues of the structures on the left except that the angle between the tetrahedron stars of the two kinds of columns is no longer equal to 45°. The real structures can be obtained by rotating all columns drawn with heavy lines in one direction and those drawn with dashed lines in the opposite direction (indicated by inscribed arrows) by about 5°. In a similar way the hypothetical structure with space group *Cmca* is obtained from the monoclinic Hf$_3$As structure if the tetrahedron star columns are not rotated by 5°.

Another geometrically related structure type of the same stoichiometry is the common Cr$_3$Si (alias β-W, W$_3$O, *A*15) structure type. This structure also contains columns of mixed tetrahedron stars but they here share atoms so that a three-dimensional framework is formed with extra majority atoms in channels. Andersson (1978) demonstrated how the two V$_3$S types can be converted into the Cr$_3$Si structure through a Hyde-rotation mechanism. In fact tetrahedron stars are commonly observed in intermetallic and other inorganic structures. As an example it can be mentioned that the Ti$_2$Ni, Th$_6$Mn$_{23}$ (closely related to the Sc$_{11}$Ir$_4$ type), CuAl$_2$ and σ-phase types, more commonly occurring with transition-metal–transition-metal compounds, also contain tetrahedron stars (see Andersson, 1978; Nyman & Andersson, 1979; Wang & Giessen, 1971).

The 5° rotation of the tetrahedron star columns in the structures on the right of Fig. 1 causes a slight change in the coordination of the minority atom. In α- and β-V$_3$S the smaller atom has 8 (+2) nearest neighbors while in compounds crystallizing with Ni$_3$P or Ti$_3$P structure types the minority atom is coordinated by 9 and 9 (+1) majority atoms respectively (Rundqvist, Andersson & Pramatus, 1979). A list of the interatomic distances in Zr$_3$Ir up to 4 Å is given in Table 2 together with $\Delta = (d - \sum r)/\sum r$, using radii for
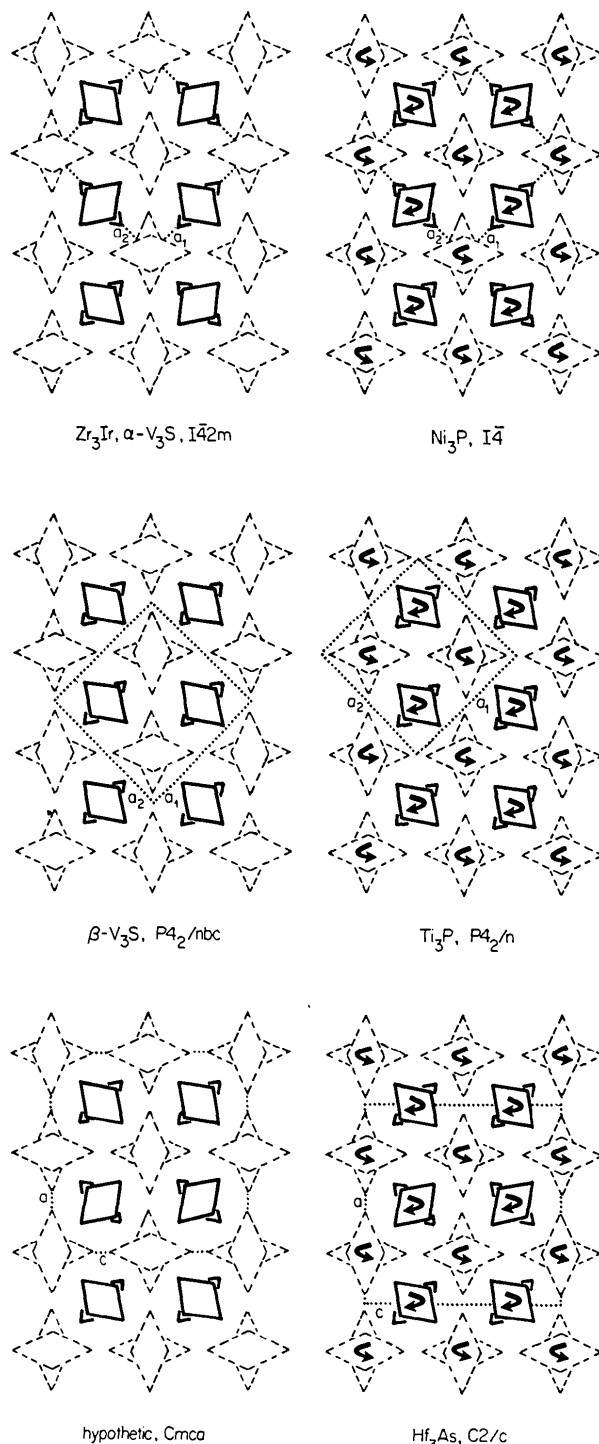

Zr$_3$Ir, α-V$_3$S, I42m   Ni$_3$P, I4

β-V$_3$S, P4$_2$/nbc   Ti$_3$P, P4$_2$/n

hypothetic, Cmca   Hf$_3$As, C2/c

Fig. 1. Schematic drawing of the arrangement of the tetrahedron star columns in the five structures belonging to the α-V$_3$S structure family and a closely related, hypothetical structure of space group *Cmca*. Star columns drawn with heavy lines are shifted by $\frac{1}{4}$ along the axis perpendicular to the plane of projection. In the structures on the right the columns should be rotated by about 5° in the sense indicated by the inscribed arrows.

Table 2. *Interatomic distances (d) up to 4 Å and*
$$\Delta = (d-\sum r)/\sum r \text{ for } Zr_3Ir$$

E.s.d.'s are given in parentheses. Atomic radii (r) used for Zr and Ir are 1·602 and 1·357 Å respectively (Teatum, Gschneidner & Waber, 1960).

	d(Å)	Δ		d(Å)	Δ
Zr(1)–2Ir(1)	2·783 (3)	−0·06	Zr(3)–2Ir(1)	2·739 (2)	−0·07
Zr(1)	2·904 (3)	−0·09	2Ir(1)	2·910 (1)	−0·02
Zr(2)	3·033 (3)	−0·05	2Zr(2)	3·093 (3)	−0·03
Zr(2)	3·262 (6)	+0·02	Zr(3)	3·140 (5)	−0·02
2Zr(3)	3·272 (4)	+0·02	2Zr(1)	3·272 (4)	+0·02
Zr(2)	3·334 (6)	+0·04	2Zr(2)	3·525 (2)	+0·10
2Zr(1)	3·397 (6)	+0·06	4Zr(3)	3·598 (2)	+0·12
2Zr(2)	3·464 (3)	+0·08			
2Zr(1)	3·599 (6)	+0·12			
			Ir(1)–2Zr(3)	2·739 (2)	−0·07
			2Zr(1)	2·783 (3)	−0·06
Zr(2)–2Ir(1)	2·783 (3)	−0·06	2Zr(2)	2·783 (3)	−0·06
Zr(1)	3·033 (3)	−0·05	2Zr(3)	2·910 (1)	−0·02
2Zr(3)	3·093 (3)	−0·03	2Zr(2)	3·481 (2)	+0·18
2Zr(2)	3·133 (6)	−0·02			
Zr(1)	3·262 (6)	+0·02			
Zr(1)	3·334 (6)	+0·04			
2Zr(1)	3·464 (3)	+0·08			
2Ir(1)	3·481 (2)	+0·18			
2Zr(3)	3·525 (2)	+0·10			

12-coordinated atoms (Teatum, Gschneidner & Waber, 1960). As expected for this structure type the Ir atom has 8 Zr atoms at distances shorter than the sum of the atomic radii, forming a distorted square antiprism, and 2 other Zr atoms at longer distances ($\Delta = 18\%$) above the square faces of the antiprism. For comparison it can be mentioned that in $Zr_{11}Os_4$, crystallizing with the $Sc_{11}Ir_4$ type (Chabot, Cenzual & Parthé, 1980), 75% of the Os atoms are 12-coordinated and of the two remaining sites occupied by Os one is at the center of a cube and the other at the center of an octahedron (the latter site making the difference between this structure type and the Th_6Mn_{23} structure type). In a similar way in $Hf_{54}Os_{17}$ 76% of the Os atoms are icosahedrally surrounded, the remaining ones having 11 nearest neighbors.

The Ti_3P and Ni_3P structure types are frequently observed with T_3M compounds where T is a transition metal and M is an element from Group 4b or 5b (see Rundqvist, Andersson & Pramatus, 1979; Waterstrat, 1981) while the β-V_3S type has so far only been observed with two compounds, namely β-V_3S (Pedersen & Grønvold, 1959) and β-Ta_3P (Phavanantha, Pontchour, Pramatus, Andersson & Rundqvist, 1978), the latter having also a low-temperature modification with Ti_3P type. The only compound known to be isotypic with Hf_3As is Ta_3As (Wang, Calvert, Gabe & Taylor, 1979). The list of compounds isotypic to α-V_3S is also short but includes chemically quite different compounds such as a sulfide: α-V_3S (Pedersen & Grønvold, 1959), two phosphides: Mo_3P (Sellberg & Rundqvist, 1965) and W_3P (Rundqvist, 1966), a compound formed by an element of Group 4b as major and Au as minor

component: Pb_3Au (Wang & Giessen, 1971), and now an alloy formed by two transition metals: Zr_3Ir.

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