

Dytterbium Decavanadate 24-Hydrate, $\text{Yb}_2\text{V}_{10}\text{O}_{28}\cdot 24\text{H}_2\text{O}$

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(Received 4 January 1984; accepted 7 December 1984)

Abstract. $M_r = 1735.85$, triclinic, $P\bar{1}$, $a = 9.287$ (5), $b = 9.821$ (5), $c = 23.33$ (2) Å, $\alpha = 99.13$ (15), $\beta = 81.51$ (15), $\gamma = 90.57$ (4)°, $V = 2077$ (3) Å³, $Z = 2$, $D_m = 2.7$, $D_x = 2.77$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 6.3$ mm⁻¹, $F(000) = 1668$, $T = 298 \pm 2$ K, $R = 4.4\%$ for 4559 independent observed reflections. The unit cell contains two independent $(\text{V}_{10}\text{O}_{28})^{6-}$ anions located on symmetry centers and four $[\text{Yb}(\text{H}_2\text{O})_8]^{3+}$ polyhedra. The V–O distances within the polyanions range between 1.578 (4) and 2.346 (5) Å. The coordination geometry at Yb^{3+} ions is a distorted square antiprism with Yb–water–O distances ranging between 2.255 (6) and 2.428 (7) Å. The 16 interstitial water molecules are inserted between layers parallel to (001) containing decavanadate groups and rare-earth polyhedra which are not in direct contact. A net of hydrogen bonds stabilizes the structure.

Introduction. Crystallographic studies on hydrated rare-earth decavanadates were undertaken as part of a more general research program on crystal chemistry and physicochemical properties of decavanadate salts (Rigotti, Punte, Rivero, Escobar & Baran, 1981). The structures of the 25-hydrate rare-earth salts (Rivero, Rigotti, Punte & Navaza, 1982, 1984) and that of the 24-hydrate compound presented here were solved in order to correlate structural changes with ionic-radius size and with the different number of water molecules of crystallization.

Experimental. $\text{Yb}_2\text{V}_{10}\text{O}_{28}\cdot 24\text{H}_2\text{O}$, isostructural with $\text{Ln}_2\text{V}_{10}\text{O}_{28}\cdot 24\text{H}_2\text{O}$ (Ln=Lu, Tm), synthesized according to the method described in a previous paper (Rigotti *et al.*, 1981) and kindly supplied by Dr E. J. Baran and co-workers, Area de Química Inorgánica, UNLP, Argentina; density measured pycnometrically. Bright-orange platelet crystal used for data collection, defined by the following planes (numbers in parentheses are the distances in mm from the crystal faces to an arbitrary

origin inside the crystal): $\pm(001)(0.21)$, $\pm(\bar{1}12)(0.16)$, $\pm(1\bar{1}2)(0.18)$ and $\pm(110)(0.11)$. Cell dimensions by least-squares refinement of 25 reflections ($17 < \theta < 25^\circ$) on an Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation, graphite monochromator. $\omega/2\theta$ scan (max. time 60 s), $\omega = (1 + 0.34 \tan\theta)^\circ$, aperture $(1 + 0.8 \tan\theta)$ mm. A hemisphere of data (h 0–10, k $\bar{1}0$ –10, l 25–25) was collected to a limit of $\sin\theta/\lambda = 0.5947$ Å⁻¹, which resulted in 4743 unique reflections, of which 4559 were observed with $I > 4\sigma(I)$. No systematic absences and $\langle E^2 - 1 \rangle$ statistic together with the Laue symmetry indicated space group $P\bar{1}$. Three standard reflections, 2.6% intensity variation. Intensities corrected for Lorentz and polarization effects; an absorption correction based on the equation of the crystal faces was applied to all observations, max. and min. corrections: 2.045 and 1.252 for $10\bar{1}$ and $7,17,6$ respectively. Positions of two independent Yb^{3+} ions obtained from a Patterson map; remaining non-hydrogen atoms from subsequent electron-density synthesis. Structure refined, with seven data per independent parameter, by block-diagonal least-squares method on $|F|$ and anisotropic thermal parameters to $R = 4.4\%$ and $wR = 5.4\%$; weighting scheme: $1/[\sigma^2(F) + 0.0074F^2]$. Max. ratio of LS shift to error 0.38, average ratio of LS shift to error 0.02; final difference map shows max. and min. heights of 0.89 and -4.06 e Å⁻³ close to Yb^{3+} ions. All calculations performed on an IBM 4331 computer with *SHELX76* (Sheldrick, 1976); atomic scattering factors for Yb^{3+} , V^{5+} and O^{1-} (used for O in the decavanadate) from Cromer & Mann (1968), those for water oxygen atoms (*OW*) supplied internally by *SHELX*.

Discussion. Final atomic positions and equivalent isotropic thermal parameters are listed in Table 1.‡

‡ Lists of structure factors, anisotropic thermal parameters, best least-squares planes, a figure showing the arrangement of different V- and O-atom types, according to Evans (1966), and bond lengths and angles within the polyanion have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39959 (40 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Interatomic distances and angles within the polyanion* show that its geometry is quite similar to that found in all the previously reported molecular structures for decavanadate salts (Evans, 1966; Swallow, Ahmed & Barnes, 1966; Saf'yanov & Belov, 1976; Saf'yanov, Kuz'min & Belov, 1978*a,b*; Durif, Averbuch-Pouchot & Guitel, 1980; Debaerdemaeker, Arrieta & Amigo, 1982; Rivero *et al.*, 1984). The decavanadate ion can be described as a section of cubic close-packed oxygen atoms with vanadium atoms in the octahedral holes. The intrinsic symmetry is *mmm* as in the structure of pascoite (Swallow *et al.*, 1966). Least-squares best planes* for the assumed *mmm* symmetry, maximum atom deviations from this symmetry (χ^2 value) and dihedral angles between these planes for the two inequivalent polyanions in diytterbium decavanadate were calculated with a modified version of the program by Ahmed & Pippy (1966). Dihedral angles between least-squares mirror planes are 89.9 (1), 90.5 (1) and 89.9 (1)° for the first decavanadate, and 90.0 (1), 90.1 (1) and 90.2 (1)° for the second. χ^2 values [$\sum(\Delta/\sigma)^2$] for the first set of planes (218.3, 111.1 and 8.4, respectively) and for the second set (1131.8, 66.0 and 9.7, respectively) indicate that the decavanadate symmetry deviates significantly from *mmm* symmetry but that the inversion center is retained. Table 2 shows V—O distances within both polyanions.

As can be seen in Fig. 1, each Yb³⁺ ion is surrounded by eight OW atoms. Central-ion—ligand distances are shown in the figure. Mean Yb(1)—OW and Yb(2)—OW distances [2.34 (4) and 2.32 (4) Å] are of the order of the sum of the ionic radius of Yb³⁺ and the van der Waals radius of OW atoms.

The symmetry of the polyhedra was examined by applying the Lippard & Russ (1967) test. The angles between intersecting trapezoidal best planes for [Yb(1)(H₂O)₈]³⁺ and [Yb(2)(H₂O)₈]³⁺ polyhedra are 84.6 (4) and 83.3 (2)° respectively. On these grounds the structures are clearly intermediate cases between the ideal antiprism (77.4°) and the ideal octahedron (90°). The additional test based on the comparison of average ligand to trapezoidal best planes distances [*ds*1(1) = 0.281, *ds*2(1) = 0.283 Å; *ds*1(2) = 0.313, *ds*2(2) = 0.336 Å] with the average ligand to best planes distances through the square faces of the antiprism [*dz*1(1) = 0.072, *dz*2(1) = 0.031 Å; *dz*1(2) = 0.035, *dz*2(2) = 0.072 Å] allows us to describe the polyhedra as distorted antiprisms. This coordination is typical of rare-earth metal ions (Cunningham, Sands & Wagner, 1967; Phillips, Sands & Wagner, 1968; Burns & Baybarz, 1972; Rivero *et al.*, 1984). Deviation from ideal symmetry may be due to the involvement of coordinated water molecules in hydrogen bonds of various strengths.

* See deposition footnote.

Table 1. Fractional positional parameters and equivalent isotropic thermal parameters with e.s.d.'s in parentheses

	x	y	z	<i>U</i> _{eq} *(Å ²)
Yb(1)	0.0686 (1)	0.0241 (1)	0.1232 (1)	0.0306 (4)
OW(29)	0.0096 (6)	-0.1922 (6)	0.0752 (3)	0.061 (7)
OW(30)	0.2007 (6)	-0.1309 (6)	0.1689 (3)	0.068 (7)
OW(31)	-0.1017 (6)	-0.0577 (6)	0.1921 (2)	0.055 (6)
OW(32)	0.1201 (6)	0.2060 (6)	0.0706 (3)	0.063 (7)
OW(33)	0.2558 (5)	0.1445 (6)	0.1685 (2)	0.047 (6)
OW(34)	-0.0355 (6)	0.2147 (5)	0.1855 (2)	0.045 (6)
OW(35)	0.2614 (6)	-0.0516 (6)	0.0524 (3)	0.059 (7)
OW(36)	-0.1349 (6)	0.0625 (6)	0.0811 (3)	0.064 (7)
Yb(2)	0.6227 (1)	0.4925 (1)	0.3804 (1)	0.0330 (4)
OW(37)	0.5383 (6)	0.3327 (7)	0.3105 (3)	0.076 (7)
OW(38)	0.6600 (6)	0.2923 (6)	0.4188 (3)	0.074 (7)
OW(39)	0.4041 (5)	0.4259 (6)	0.4279 (3)	0.057 (6)
OW(40)	0.7457 (7)	0.6652 (6)	0.3346 (3)	0.063 (7)
OW(41)	0.8099 (6)	0.5449 (6)	0.4350 (3)	0.062 (7)
OW(42)	0.5513 (6)	0.6757 (6)	0.4499 (3)	0.066 (7)
OW(43)	0.8186 (6)	0.3874 (6)	0.3171 (3)	0.063 (7)
OW(44)	0.4410 (7)	0.6077 (7)	0.3405 (2)	0.074 (7)
OW(45)	0.6709 (6)	0.2579 (6)	0.2028 (2)	0.057 (6)
OW(46)	0.5140 (7)	0.0289 (7)	0.1734 (3)	0.098 (8)
OW(47)	0.0698 (6)	0.4797 (8)	0.1986 (3)	0.082 (8)
OW(48)	0.8411 (7)	0.6777 (6)	0.2177 (3)	0.076 (7)
OW(49)	0.8024 (8)	0.0885 (7)	0.3007 (3)	0.114 (9)
OW(50)	0.2635 (7)	0.2508 (7)	0.2921 (3)	0.087 (8)
OW(51)	0.0938 (6)	0.4940 (7)	0.3112 (2)	0.068 (7)
OW(52)	0.534 (1)	0.897 (1)	0.2649 (5)	0.20 (2)
V(1)	0.5196 (1)	0.2819 (1)	0.0543 (1)	0.022 (1)
V(2)	0.3956 (1)	0.2776 (1)	-0.0619 (1)	0.025 (1)
V(3)	0.7791 (1)	0.4687 (1)	0.0783 (1)	0.026 (1)
V(4)	0.6637 (1)	0.4646 (1)	-0.0382 (1)	0.018 (1)
V(5)	0.4739 (1)	0.5367 (1)	0.1503 (1)	0.028 (1)
O(1)	0.5192 (6)	0.8791 (6)	-0.0516 (2)	0.056 (6)
O(2)	0.2914 (5)	0.7096 (5)	-0.0677 (2)	0.044 (5)
O(3)	0.4384 (5)	0.3517 (5)	0.1292 (2)	0.044 (6)
O(4)	0.4146 (5)	0.7153 (4)	0.0311 (2)	0.029 (5)
O(5)	0.6589 (5)	0.6590 (5)	-0.0248 (2)	0.037 (5)
O(6)	0.4481 (5)	0.4989 (5)	-0.0495 (2)	0.028 (5)
O(7)	0.6405 (6)	0.8820 (6)	0.0630 (3)	0.060 (6)
O(8)	0.5116 (5)	0.7154 (5)	0.1346 (2)	0.039 (5)
O(9)	0.7791 (5)	0.6529 (5)	0.0727 (2)	0.037 (5)
O(10)	0.0642 (5)	0.5577 (6)	-0.0931 (2)	0.054 (6)
O(11)	0.6657 (5)	0.5041 (5)	0.1518 (2)	0.035 (5)
O(12)	0.1829 (5)	0.5613 (5)	0.0103 (2)	0.033 (5)
O(13)	0.2916 (5)	0.5623 (5)	0.1119 (2)	0.042 (6)
O(14)	0.4071 (6)	0.5681 (7)	0.2180 (2)	0.067 (7)
V(6)	0.0668 (1)	0.1925 (1)	0.4304 (1)	0.028 (1)
V(7)	0.1476 (1)	0.7657 (1)	0.4558 (1)	0.026 (1)
V(8)	0.3423 (1)	0.0097 (1)	0.4208 (1)	0.034 (1)
V(9)	0.8670 (1)	0.9483 (1)	0.4626 (1)	0.024 (1)
V(10)	0.0967 (1)	0.9061 (1)	0.3508 (1)	0.034 (1)
O(15)	0.0328 (6)	0.3449 (6)	0.4216 (2)	0.055 (6)
O(16)	0.2654 (5)	0.1834 (5)	0.4191 (2)	0.046 (6)
O(17)	0.0507 (6)	0.0926 (5)	0.3589 (2)	0.045 (5)
O(18)	0.9339 (5)	0.7783 (5)	0.4829 (2)	0.035 (5)
O(19)	0.8664 (5)	0.1425 (5)	0.4621 (2)	0.033 (5)
O(20)	0.0942 (5)	0.9814 (5)	0.4509 (2)	0.034 (5)
O(21)	0.1811 (6)	0.6150 (6)	0.4660 (2)	0.049 (6)
O(22)	0.1178 (5)	0.7430 (5)	0.3805 (2)	0.031 (5)
O(23)	0.3331 (5)	0.8309 (5)	0.4400 (2)	0.035 (5)
O(24)	0.0831 (6)	0.8515 (6)	0.2845 (3)	0.078 (7)
O(25)	0.2888 (6)	0.9443 (6)	0.3486 (2)	0.060 (6)
O(26)	0.5124 (6)	1.0364 (6)	0.4053 (3)	0.074 (7)
O(27)	0.6932 (6)	0.9293 (5)	0.4911 (2)	0.048 (6)
O(28)	0.8836 (5)	0.8942 (5)	0.3892 (2)	0.040 (5)

* Defined according to Hamilton (1959).

The decavanadate polyanions and the rare-earth coordination polyhedra are less distorted in the title compound than in the isostructural yttrium compound, Y₂V₁₀O₂₈·24H₂O (Saf'yanov *et al.*, 1978*a*).

Fig. 2 shows a stereoscopic view of the structure. Layers of decavanadate polyanions and Yb coordination polyhedra are linked solely through hydrogen bonds of interstitial water molecules. The structure is stabilized by a network of hydrogen bonds both within

Table 2. *Interatomic distances* (Å)

Yb(1) decavanadate			
V(1)—O(1)	1.612 (5)	V(4)—O(4)	1.926 (4)
V(1)—O(2)	1.826 (4)	V(4)—O(5)	1.885 (5)
V(1)—O(3)	1.825 (5)	V(4)—O(6)	2.130 (5)
V(1)—O(4)	2.000 (4)	V(4)—O(6')	2.096 (5)
V(1)—O(5)	2.011 (5)	V(4)—O(12)	1.688 (4)
V(1)—O(6)	2.189 (5)	V(4)—O(13)	1.688 (4)
V(2)—O(4)	1.996 (5)	V(5)—O(3)	1.845 (5)
V(2)—O(5)	2.008 (5)	V(5)—O(6)	2.329 (5)
V(2)—O(6)	2.206 (5)	V(5)—O(8)	1.869 (5)
V(2)—O(7)	1.596 (5)	V(5)—O(11)	1.820 (5)
V(2)—O(8)	1.797 (5)	V(5)—O(13)	2.064 (5)
V(2)—O(9)	1.833 (5)	V(5)—O(14)	1.592 (5)
V(3)—O(2)	1.856 (4)		
V(3)—O(6)	2.346 (5)		
V(3)—O(9)	1.834 (5)		
V(3)—O(10)	1.578 (4)		
V(3)—O(11)	1.859 (4)		
V(3)—O(12)	2.019 (5)		
Yb(2) decavanadate			
V(6)—O(15)	1.585 (6)	V(9)—O(18)	1.938 (5)
V(6)—O(16)	1.825 (5)	V(9)—O(19)	1.909 (5)
V(6)—O(17)	1.823 (5)	V(9)—O(20)	2.109 (5)
V(6)—O(18)	1.996 (5)	V(9)—O(20')	2.116 (5)
V(6)—O(19)	1.985 (5)	V(9)—O(27)	1.672 (5)
V(6)—O(20)	2.225 (5)	V(9)—O(28)	1.695 (5)
V(7)—O(18)	1.990 (5)	V(10)—O(17)	1.858 (5)
V(7)—O(19)	1.969 (5)	V(10)—O(20)	2.331 (5)
V(7)—O(20)	2.205 (5)	V(10)—O(22)	1.866 (5)
V(7)—O(21)	1.577 (6)	V(10)—O(24)	1.579 (6)
V(7)—O(22)	1.798 (5)	V(10)—O(25)	1.815 (5)
V(7)—O(23)	1.839 (5)	V(10)—O(28)	2.058 (5)
V(8)—O(16)	1.865 (5)		
V(8)—O(20)	2.334 (5)		
V(8)—O(23)	1.878 (5)		
V(8)—O(25)	1.842 (6)		
V(8)—O(26)	1.597 (5)		
V(8)—O(27)	2.027 (5)		

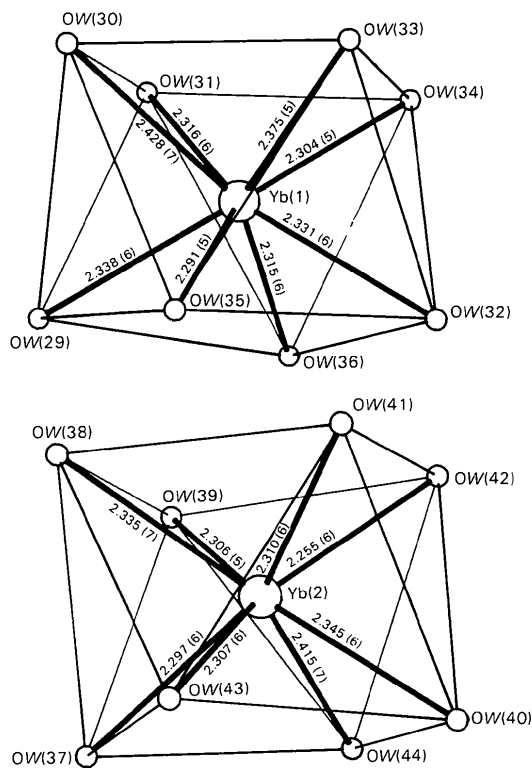


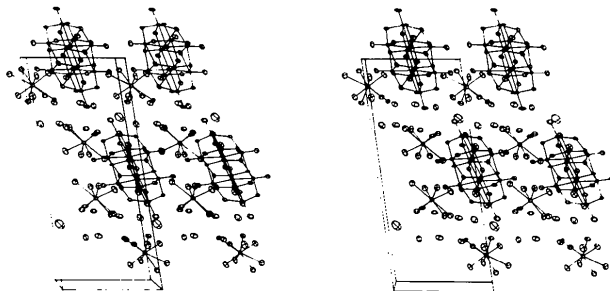
Fig. 1. Yb—OW distances (Å) in the YbOW polyhedra. E.s.d.'s are in parentheses.

the layers and between them. The existence of these bonds is indicated by the distances found between water molecules and their nearest neighbors. This fact is partially confirmed by the presence of peaks that could be interpreted as protons, in approximately the expected positions in the final difference map. The O—OW and OW—OW distances range between 2.606 (8) and 3.164 (8) Å.

Analysis of the molecular structures of all the solved rare-earth decavanadates (Saf'yanov, Kuz'min & Belov, 1979; Rivero *et al.*, 1982, 1984) shows that, despite the different symmetries and unit cells adopted, all have a layered structure with weak links between layers, giving good cleavage in that direction. All rare-earth coordination polyhedra are distorted capped trigonal prisms but differences are found in coordination numbers. La, Ce, Pr, Nd and Sm are nine-coordinate, while the remaining rare-earth cations are eight-coordinate. The cation coordination polyhedra and the decavanadate ions are normally linked only by hydrogen bonds. The exceptions are $\text{Ln}_2\text{V}_{10}\text{O}_{28}\cdot 20\text{H}_2\text{O}$ (Ln=La, Ce) (Saf'yanov *et al.*, 1978*b*; Rigotti *et al.*, 1981), in which neutral $[(\text{Ln}_2\cdot 7\text{H}_2\text{O})\text{V}_{10}\text{O}_{28}]$ complexes occur.

Differences in the crystal structures and coordination polyhedra from La to Eu may be attributed to changes in the ionic radius according to Wells (1975), Moeller (1975) and Nassimbeni, Wright, van Niekerk & McCallum (1979). However, the existence of two diyttrium decavanadate hydrates, one (Saf'yanov *et al.*, 1978*a*) isostructural with $\text{Yb}_2\text{V}_{10}\text{O}_{28}\cdot 24\text{H}_2\text{O}$ and the other (Rivero *et al.*, 1982) isostructural with $\text{Ln}_2\text{V}_{10}\text{O}_{28}\cdot 25\text{H}_2\text{O}$ (Ln=Eu, Gd, Tb, Dy, Ho, Er) (Rivero *et al.*, 1984), together with crystal-optical- and thermal-properties studies on the 24-, 25- and 28-hydrates of rare-earth decavanadates (Glazyrin & Ivakin, 1964; Ivakin, Ignat'eva & Glazyrin, 1967), seem to contradict the above statement.

Thus it may be concluded that rare-earth decavanadates exhibit at least four crystallographic forms: $\text{Ln}_2\text{V}_{10}\text{O}_{28}\cdot 20\text{H}_2\text{O}$ (Ln=La, Ce); $\text{Ln}_2\text{V}_{10}\text{O}_{28}\cdot 28\text{H}_2\text{O}$ (Ln=La, Ce, Pr, Nd, Sm); $\text{Ln}_2\text{V}_{10}\text{O}_{28}\cdot 25\text{H}_2\text{O}$ (Ln=Eu,

Fig. 2. Stereoscopic view of the structure down a^* , with the b axis horizontal.

Gd,Tb,Dy,Ho,Er,Yb,Y) and $\text{Ln}_2\text{V}_{10}\text{O}_{28}\cdot 24\text{H}_2\text{O}$ (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.

The authors thank Dr P. Charpin for helpful discussions, and CONICET, CICPBA and SUBCYT (R. Argentina) for financial support.

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Zr₃Ir with Tetragonal α -V₃S Structure

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(Received 7 January 1985; accepted 1 February 1985)

Abstract. $M_r = 465.86$, $I\bar{4}32$, $I\bar{4}2m$, $a = 10.788$ (2), $c = 5.662$ (1) Å, $V = 658.9$ (2) Å³, $Z = 8$, $D_x = 9.39$ Mg m⁻³, $\text{Mo } K\alpha$, $\lambda = 0.71069$ 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 & Kudrjavitsev, 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.