



ELSEVIER

Journal of Alloys and Compounds 234 (1996) 12-18

Journal of  
ALLOYS  
AND COMPOUNDS

# Synthesis, properties and crystal structure of $Zr_6Zn_{23}Si$ with “filled” $Th_6Mn_{23}$ type structure

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Received 21 June 1995

## Abstract

The new compound  $Zr_6Zn_{23}Si$  has been prepared by a solid state reaction of a zirconium-zinc alloy and silicon. It is weakly diamagnetic and this is interpreted as Pauli paramagnetism, which is overcompensated by the core diamagnetism. Its crystal structure has been determined from single-crystal diffractometer data:  $Fm\bar{3}m$ ,  $a = 1238.5(1)$  pm,  $Z = 4$ ,  $R = 0.022$  for 215 structure factors and 17 variable parameters. The Zr and Zn atoms occupy the positions of the Th and Mn atoms in  $Th_6Mn_{23}$ , while the Si atoms are situated at octahedral voids of that structure formed by the Zr atoms. Thus the atomic positions of  $Zr_6Zn_{23}Si$  correspond to those of  $Sc_{11}Ir_4$  (i.e.  $Sc_6Sc_{16}Ir_7Ir$ ). Various void positions of these structures correspond to hydrogen sites in previously reported rare earth (R) transition metal (T) hydrides  $R_6T_{23}H_{75-x}$ .

**Keywords:** Crystal chemistry; Intermetallics; Pauli paramagnetism

## 1. Introduction

We have recently reported on the properties and crystal structures of  $Ti_3Zn_{22}$ ,  $TiZn_{16}$  [1],  $Zr_5Zn_{39}$  and  $ZrZn_{22}$  [2]. While attempting to prepare the as-yet poorly characterized phase “ $ZrZn_3$ ” [3] by annealing in evacuated silica tubes, we obtained a ternary silicon-containing phase as a byproduct. Subsequently single crystals of this compound were grown in a zinc flux by deliberately adding elemental silicon. In the present paper, we report the preparation, the magnetic properties, and the crystal structure of this compound.

## 2. Sample preparation and lattice constants

The preparation of  $Zr_6Zn_{23}Si$  by direct reaction of the elemental components is difficult because zirconium reacts easily with silicon to form the very stable impurity phase  $Zr_5Si_3$  [4]. Good results are obtained by starting from powders of a zirconium-zinc alloy with a small amount of silicon.

Starting materials were powders of zirconium, zinc and silicon, as well as zinc granules, all with nominal purities greater than 99.9%. The zirconium-zinc alloys with the composition  $Zr:Zn = 1:3$  were first prepared by annealing cold-pressed pellets at 620°C for one week with one intermittent grinding. The resulting products were mixed with granules of zinc and silicon powder in the atomic ratio  $Zr:Zn:Si = 4.39:95.24:0.37$  and placed in alumina containers, which were sealed in silica tubes under argon. The samples were heated gradually to 910°C, where they were kept for one week. They were then cooled to 760°C at a rate of 2°C  $h^{-1}$ , followed by annealing at that temperature for one week and quenching in cold water.

After this treatment well-developed crystals of  $Zr_6Zn_{23}Si$  were found in the crushed sample together with the microcrystalline impurity phase  $ZrZn_{22}$ . The crystals had the form of rhombic dodecahedra with {110} faces and with dimensions up to  $0.2 \times 0.2 \times 0.2$  mm<sup>3</sup>. They are grey with metallic lustre and stable in air for long periods of time, but they are slowly attacked by diluted hydrochloric acid. Energy-dispersive X-ray fluorescence analyses in a scanning electron microscope were compatible with the ideal composition and did not reveal any impurity elements heavier than sodium.

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The crystals of  $Zr_6Zn_{23}Si$  are easily ground to powders. Guinier powder patterns were recorded with  $\alpha$ -quartz ( $a = 491.30$  pm,  $c = 540.46$  pm) as an internal standard, and the lattice constants were refined by least-squares fits. They are in good agreement with those obtained from the X-ray four-circle diffractometer data (Table 1).

### 3. Magnetic susceptibilities

Selected single crystals of  $Zr_6Zn_{23}Si$  were investigated with a superconducting quantum interference device magnetometer in the temperature range between 20 and 300 K at magnetic flux densities up to 5 T. The magnetic susceptibilities of that sample were slightly field dependent. This was ascribed to a minor amount of an unknown ferromagnetic impurity phase with a Curie point above room temperature. Therefore the data were extrapolated to infinite magnetic field strengths (Fig. 1). They exhibit large scatter because of the small amount of the sample. Nevertheless, it can be seen that the susceptibility values above 100 K have little temperature dependence. The mean values are negative. Because of its very high zinc content we expect  $Zr_6Zn_{23}Si$  to be a metallic conductor. Therefore we interpret the nearly temperature-independent magnetic susceptibility data above 100 K as being due to a temperature-independent Pauli paramagnetism of that compound, which is overcompensated by the core diamagnetism. The upturn of the susceptibilities at temperatures below 100 K may be ascribed to a minor amount of another unknown impurity phase, which is paramagnetic in the tempera-

ture range investigated by us. A likely possibility for this impurity is  $ZrZn_2$ , which has Curie temperatures of less than 35 K, depending on its composition [5–7].

### 4. Structure determination

Single crystals of  $Zr_6Zn_{23}Si$  were examined in a Buerger precession camera. They exhibit the Laue symmetry  $m\bar{3}m$  and the only systematic extinctions of a face-centered lattice were compatible with the space groups  $F432$ ,  $F\bar{4}3m$  and  $Fm\bar{3}m$ , of which the group with the highest symmetry  $Fm\bar{3}m$  was found to be correct during the structure refinements.

The X-ray diffraction intensity data were recorded on an automated four-circle diffractometer with graphite-monochromated Mo  $K\alpha$  radiation and a scintillation counter with pulse-height discrimination. The background was determined on both sides of each  $\theta$ – $2\theta$  scan. An empirical absorption correction was made on the basis of  $\psi$  scans. The crystallographic data and some results are summarized in Table 1.

From the dimensions of the unit cell it was originally guessed that  $Zr_6Zn_{23}Si$  might have a  $Th_6Mn_{23}$ -type structure and the positional parameters of  $Th_6Mn_{23}$  [8] were used as the starting parameters for the zirconium and zinc atoms in  $Zr_6Zn_{23}Si$ . The silicon position was obtained from a difference Fourier synthesis. The structure was refined by a full-matrix least-squares

Table 1  
Crystallographic data for  $Zr_6Zn_{23}Si$ <sup>a</sup>

	$Zr_6Zn_{22.915(8)}Si$
Composition	$Zr_6Zn_{22.915(8)}Si$
Crystal dimensions ( $\mu\text{m}^3$ )	$40 \times 40 \times 40$
Space group	$Fm\bar{3}m$ (no. 225)
Lattice constants	
From powder data	
$a$ (pm)	1238.5(1)
$V$ ( $\text{nm}^3$ )	1.8997
From single-crystal data	
$a$ (pm)	1238.4(1)
$V$ ( $\text{nm}^3$ )	1.8993
Formula units per cell $Z$	4
Formula mass	2073.4
Calculated density $\rho$ ( $\text{g cm}^{-3}$ )	7.25
$\theta$ – $2\theta$ scans up to	$2\theta = 80^\circ$
Range in $hkl$	$\pm 22, \pm 22, 0-22$
Total number of reflections	6044
Unique reflections	350
Inner residual $R_i$	0.047
Reflections with $I > 1\sigma(I)$	215
Highest to lowest transmission ratio	1.19
Number of variables	17
Secondary extinction coefficient	$7.1 \times 10^{-7}$
Conventional residual $R$	0.022
Weighted residual $R_w$	0.017

<sup>a</sup> Standard deviations in the positions of the least significant digits are given in parentheses throughout the paper.

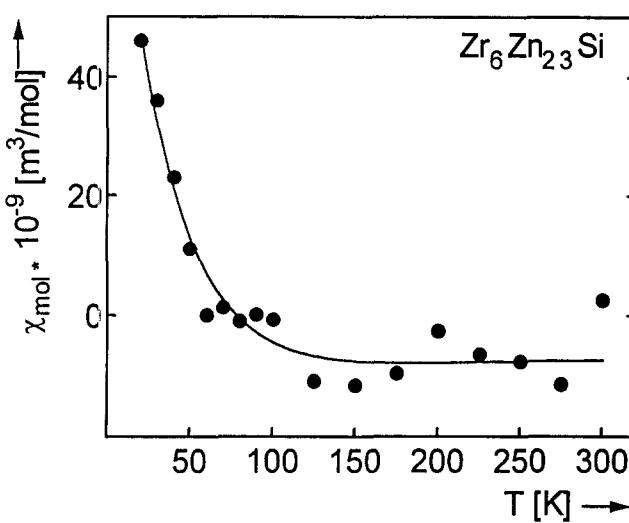


Fig. 1. Magnetic susceptibility of  $Zr_6Zn_{23}Si$  as a function of temperature. The upturn of the data at low temperatures is ascribed to an impurity phase. —, guide for the eye.

Table 2  
Atomic parameters of  $Zr_6Zn_{23}Si$ <sup>a</sup>

Atom	Occupancy	$Fm\bar{3}m$	$x$	$y$	$z$	$B_{eq} (\times 10^{-2} \text{ nm}^2)$
Zr	1	24e	0.21041(7)	0	0	0.478(7)
Zn1	1	32f	0.16437(4)	x	x	0.609(3)
Zn2	1	32f	0.37723(4)	x	x	0.776(3)
Zn3	1	24d	0	1/4	1/4	0.537(8)
Zn4	0.915(8)	4b	1/2	1/2	1/2	1.03(1)
Si	1	4a	0	0	0	0.87(3)

<sup>a</sup> The last column contains the equivalent isotropic B values. The Zn4 position was found to be partially occupied and therefore the exact formula of the compound is  $Zr_6Zn_{22.915(8)}Si$ .

Table 3  
Interatomic distances (picometres) in  $Zr_6Zn_{23}Si$ <sup>a</sup>

Zr:	1Si	260.6	Zn2:	1Zn4	263.4
	4Zn1	293.5		3Zn3	269.8
	4Zn2	298.2		3Zn1	273.5
	4Zn3	313.5		3Zr	298.2
	1Zn4	358.7		3Zn2	304.1
	4Zr	368.5	Zn3:	4Zn1	252.9
Zn1:	3Zn3	252.9		4Zn2	269.8
	3Zn2	273.5		4Zr	313.5
	3Zr	293.5	Zn4:	8Zn2	263.4
	3Zn1	300.0		6Zr	358.7
	[1Si]	352.6	Si:	6Zr	260.6
				[8Zn1]	352.6

<sup>a</sup> All distances shorter than 400 pm are listed. All standard deviations are 0.1 pm or less. The distances set in brackets are too long to be considered as bonding.

program of the SOD package [9] with atomic scattering factors [10], corrected for anomalous dispersion [11]. The weighting scheme included a term which accounted for the counting statistics and a parameter correcting for isotropic secondary extinction was optimized. To check for deviations from the ideal composition all occupancy parameters were allowed to vary along with the thermal parameters, while the scale factors were held constant. The resulting occupancies were 1.002(2) for Zr, 0.997(2) for Zn1, 0.997(2) for Zn2, 1.006(3) for Zn3, 0.912(8) for Zn4 and 0.99(2) for Si. Thus only the Zn4 position exhibited a significant deviation from the full occupancy. Accordingly, in the last least-squares cycles all occupancy parameters were assumed to be ideal with the exception of the

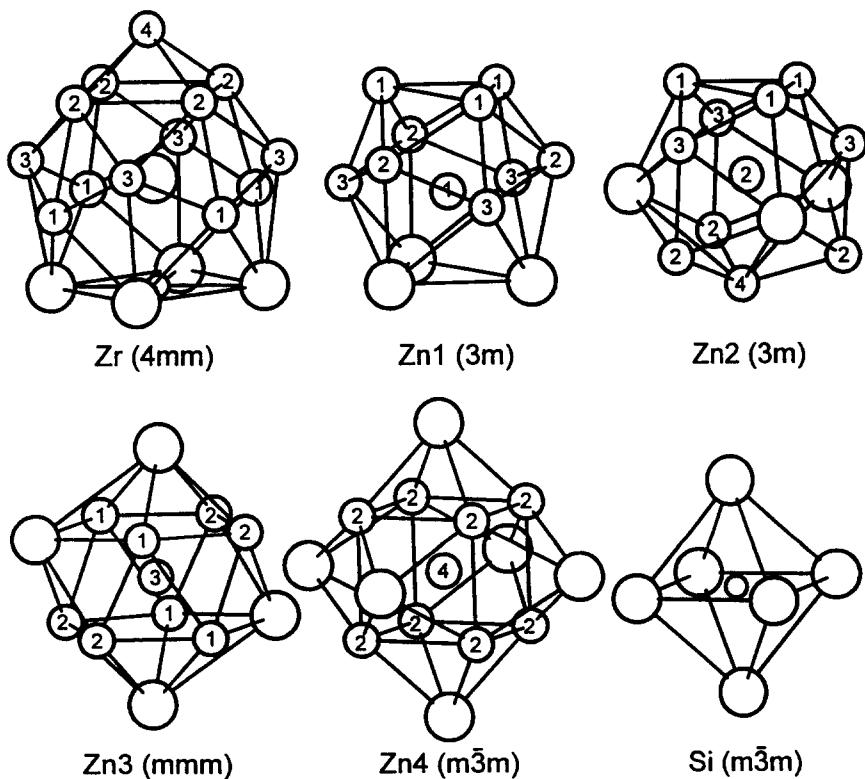


Fig. 2. Coordination polyhedra in the structure of  $Zr_6Zn_{23}Si$ . Single-digit numbers correspond to the atom designations. The site symmetries of the central atoms are also indicated.

Zn4 position, which was finally refined to an occupancy of 91.5(8)%. Therefore the exact composition of the crystal used for the structure determination was  $\text{Zr}_6\text{Zn}_{22.915(8)}\text{Si}$ . The refinement resulted in the conventional and weighted residuals  $R = 0.022$  and  $R_w = 0.017$  for 17 variable parameters and 215 structure

factors. A final difference Fourier synthesis revealed values of  $\pm 0.5e \text{ \AA}^{-3}$  as the highest and lowest electron densities. The atomic parameters and interatomic distances are given in Tables 2 and 3. Listings of the anisotropic thermal parameters and the structure factors are available from the authors.

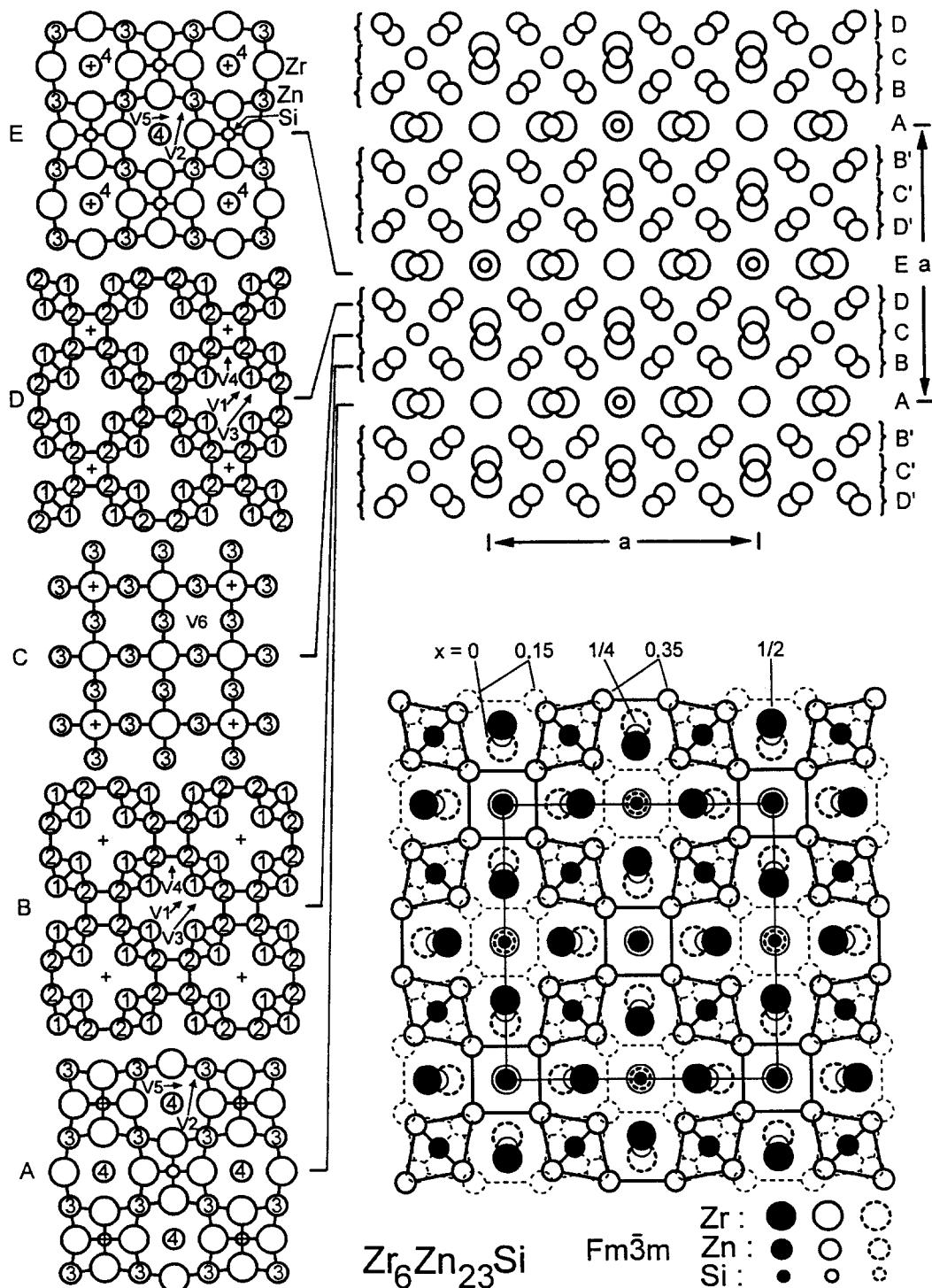


Fig. 3. Crystal structure of  $\text{Zr}_6\text{Zn}_{23}\text{Si}$ . Atoms may be visualized as situated on the atomic layers A–E. These layers are shown separately (at a slightly reduced scale) on the left-hand side and superimposed at the lower right-hand corner of the figure. Some positions of the voids V1–V6 are indicated. Single-digit numbers and crosses correspond to the atom designations and the origin positions of the cell. The silicon atoms, situated at the corners and face-centered positions of the f.c.c. cell, are sometimes hidden under the large zirconium atoms.

## 5. Discussion

In the structure of  $Zr_6Zn_{23}Si$  all metal atoms have high coordination numbers, as is usually the case for intermetallic phases. The zirconium atoms are coordinated by one silicon, thirteen zinc and four zirconium atoms. The Zr–Zr distances of 368.5 pm are rather large, considering the metallic radius of zirconium for the coordination number (CN) 12 of 160 pm. Nevertheless, if one discounts these zirconium neighbours the coordination polyhedron of the zirconium atom would look rather incomplete (Fig. 2). The Zr–Zn distances cover the range between 293 pm and 359 pm. This range is comparable with the range from 291 to 346 pm in  $Zr_5Zn_{39}$  [2]. The zinc atoms occupy four different atomic sites with CNs 12 (Zn1, Zn3), 13 (Zn2) and 14 (Zn4).

The silicon atoms occupy a site which is octahedrally coordinated by zirconium atoms. The Zr–Si distances of 260.6 pm are rather short. This has to do with the low CN of this site. In the binary zirconium silicides  $Zr_2Si$  [12],  $ZrSi$  [13],  $Zr_5Si_4$  [14] and  $ZrSi_2$  [15] the silicon atoms have CNs varying between 8 and 10, and as a consequence the Zr–Si distances in these binary zirconium silicides are greater. In the sequence as we listed them above the shortest Zr–Si distances (with the CN of the silicon atoms in parentheses) are 282 pm (CN 10), 274 pm (CN 9), 260 pm (CN 9), 271 pm (CN 8). Thus, with the exception of the one short Zr–Si distance of 260 pm in  $Zr_5Si_4$  (which is not very accurate) these distances are all greater than the distance of 260.6 pm in the present compound. The octahedral coordination and the shortness of this distance might suggest the occupancy of this site by a lighter interstitial atom; however, this would be in complete contradiction to the result of the refinement of the occupancy factor which was 99(2)%.

The structure of  $Zr_6Zn_{23}Si$  (Fig. 3) may be regarded

as a “filled”  $Th_6Mn_{23}$  structure, where the metal positions correspond to each other, while the position of the silicon atom is unoccupied in  $Th_6Mn_{23}$ . A filled  $Th_6Mn_{23}$  structure, where all atomic positions correspond to those of  $Zr_6Zn_{23}Si$ , was reported earlier for  $Sc_{11}Ir_4$  [16] as may be expressed by the formula  $Sc_6Sc_{16}Ir_7Ir$ . This indicates that some of the large scandium atoms occupy the positions of the small manganese atoms of  $Th_6Mn_{23}$ . Other filled  $Th_6Mn_{23}$  structures were reported for various rare earth (R) manganese and iron (T) hydrides (and deuterides)  $R_6T_{23}H_x$ , where  $x$  may be as high as 23 [17–19]. The positions of the hydrogen (deuterium) atoms have been determined by neutron powder diffraction (Table 4, Fig. 4). With the exception of the silicon position they are not occupied in  $Zr_6Zn_{23}Si$ . We have labelled these void positions V1–V6. The “coordination” of these void positions in  $Zr_6Zn_{23}Si$  are listed in Table 5. It can be seen that these voids are large enough to accommodate small “interstitial” atoms such as carbon, nitrogen or oxygen. Our final difference Fourier synthesis showed that the residual electron densities were all less than  $0.5e\text{ \AA}^{-3}$ . For the occupancy of the void positions by carbon or oxygen atoms electron densities of about 12 or  $16e\text{ \AA}^{-3}$  would have been expected.

The structure of  $Zr_6Zn_{23}Si$  is not easy to visualize. In Fig. 3 we show the structure as being composed of various atomic layers A–E. The atoms of the equivalent layers A and E are situated on mirror planes. The other (somewhat arbitrarily chosen) layers are puckered. The equivalent layers B and D contain only zinc atoms, the layer C is made up of zirconium and zinc atoms, while the layers A and E consist of all three atomic species. The positions of some voids are also indicated. Not all of these can be occupied at the same time, since the distances V1–V3 and V2–V5 are rather short (Table 5). Therefore, from space considerations

Table 4  
Compounds which might be considered to crystallize with a “filled”  $Th_6Mn_{23}$ -type structure<sup>a</sup>

Compound	24e	32f	32f	24d	4b	4a	32f	48i	96k	96j	96j	8c	Ref.
$Zr_6Zn_{23}Si$	Zr (21,00,00)	Zn1 (16,16,16)	Zn2 (38,38,38)	Zn3 (00,25,25)	Zn4 (92%) (50,50,50)	Si (00,00,00)	V1 (08,08,08)	V2 (50,16,16)	V3 (15,15,03)	V4 (00,20,39)	V5 (00,04,36)	V6 (25,25,25)	This work
$Th_6Mn_{23}$	Th (20,00,00)	Mn4 (18,18,18)	Mn3 (38,38,38)	Mn2 (00,25,25)	Mn1 (50,50,50)								[8]
$Ir_4Sc_{11}$	Sc1 (20,00,00)	Sc3 (16,16,16)	Sc2 (38,38,38)	Ir3 (00,25,25)	Ir2 (50,50,50)	Ir1 (00,00,00)							[16]
$Y_6Mn_{23}D_8$	Y (23,00,00)	Mn4 (18,18,18)	Mn3 (38,38,38)	Mn2 (00,25,25)	Mn1 (50,50,50)	D1 (63%) (00,00,00)	D2 (96%) (10,10,10)						[17]
$Th_6Mn_{23}D_{16}$	Th (21,00,00)	Mn3 (18,18,18)	Mn4 (37,37,37)	Mn2 (00,25,25)	Mn1 (50,50,50)	D1 (10%) (00,00,00)	D2 (10,10,10)	D3 (68%) (50,14,14)					[18]
$Ho_6Fe_{23}D_8$	Ho (21,00,00)	Fe3 (18,18,18)	Fe4 (38,38,38)	Fe2 (00,25,25)	Fe1 (50,50,50)	D1 (23%) –	D2 (10,10,10)	D2 (0.7%) –	D3 (38%) (16,16,03)				[19]
$Y_6Mn_{23}D_{18}$	Y (23,00,00)	Mn4 (18,18,18)	Mn3 (38,38,38)	Mn2 (00,25,25)	Mn1 (50,50,50)	D1 (00,00,00)	D2 (09,09,09)	–	–	D3 (38%) (00,17,35)			[17]
$Y_6Mn_{23}D_{23}$	Y (24,00,00)	Mn4 (19,19,19)	Mn3 (38,38,38)	Mn2 (00,25,25)	Mn1 (50,50,50)	D1 (00,00,00)	D2 (10,10,10)	D4 (18%) –	D3 (40%) (15,15,01)	D4 (18%) (00,17,37)			[17]
$Ho_6Fe_{23}D_{16}$	Ho (21,00,00)	Fe3 (18,18,18)	Fe4 (37,37,37)	Fe2 (00,25,25)	Fe1 (50,50,50)	D1 (23%) –	D2 (10,10,10)	D4 (1.5%) –	D2 (5%) (16,16,05)	D3 (3%) (00,14,34)	D3 (3%) (00,08,39)		[19]

<sup>a</sup> Atomic parameters ( $x, y, z$ ) are listed in hundredths. For partially occupied atomic sites the occupancy parameters are given in parentheses. For  $Zr_6Zn_{23}Si$  the positions of the vacant sites V1–V6 are also listed.

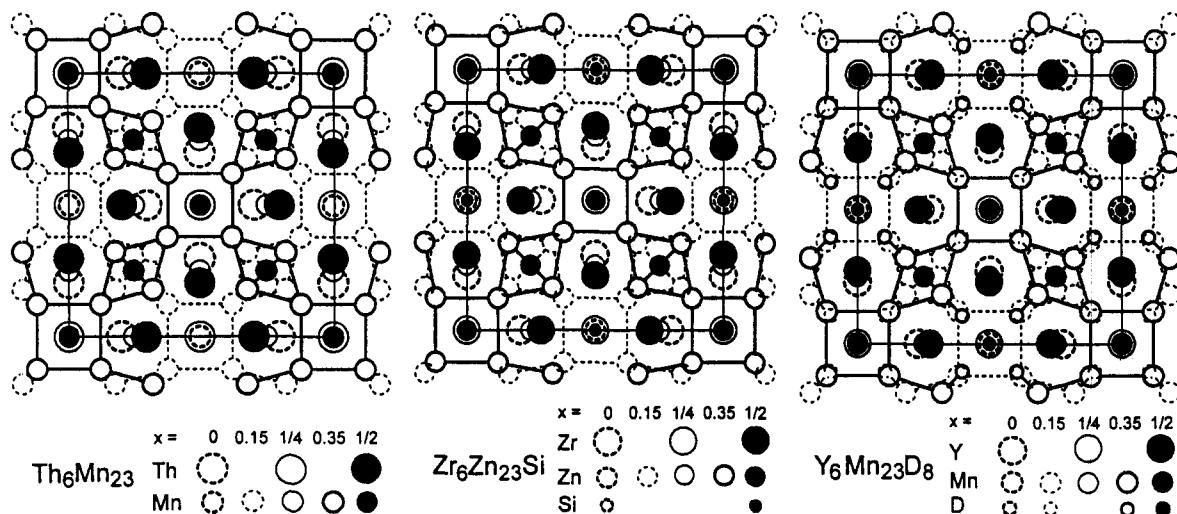


Fig. 4. The crystal structure of  $Zr_6Zn_{23}Si$  as compared with the closely related structures of  $Th_6Mn_{23}$  and  $Y_6Mn_{23}D_8$ . Only the lower halves of the cubic cells are shown. Some silicon and deuterium positions are hidden under the large metal atoms.

Table 5  
Location and coordination of unoccupied sites (voids V) in the structure of  $Zr_6Zn_{23}Si$  (distances in picometres)

	Site	x	y	z	
V1	32f	0.082		x	
V2	48i	1/2		0.157	y
V3	96k	0.154		x	0.027
V4	96j	0		0.200	0.386
V5	96j	0		0.039	0.355
V6	8c	1/4		1/4	1/4
V1:	1V3	143			V4: 1Zn3 180
	1Si	176			2Zn2 180
	1Zn1	176			1Zr 180
	3Zr	214			V5: 1V2 146
V2:	1V5	146			1Zr 186
	2Zn2	163			1Zn4 186
	1Zn3	163			2Zn2 186
	2Zr	255			V6: 4Zn1 184
V3:	1V1	143			
	1Zn1	171			
	1Zn3	171			
	2Zr	206			

the formulae for the completely filled structures would be  $Th_6Mn_{23}H_{75}$  and  $Zr_6Zn_{23}SiX_{74}$ .

We have argued before [1,2] that the voids of the intermetallic phases with high zinc content might be needed to accommodate non-bonding electrons of the zinc atoms. In nearly isotypic compounds with lower electron count these voids could be filled with interstitial atoms. Such correspondences are known for  $LaMn_{17}C_{2-x}$  and  $BaCd_{11}$  [20],  $Pr_2Mn_{17}C_{3-x}$  and  $Th_2Zn_{17}$  [21],  $UW_4C_4$  and  $MoNi_4$  [22], as well as for  $Tb_2Mn_{17}C_{3-x}$  and  $Th_2Ni_{17}$  [23]. Some further examples were listed more recently. In all of these examples the average valence electron number of the metal atoms (AVENOMA value [22,24]) is higher for the

unfilled binary compound than for the filled ternary compound. At the first sight the correspondence of  $Th_6Mn_{23}$  and  $Zr_6Zn_{23}Si$  seems to be an example of the opposite kind. Here the AVENOMA value for the unfilled compound  $Th_6Mn_{23}$  ( $6 \times 4 + 23 \times 7 = 185$ ) is lower than the corresponding value for the filled compound  $Zr_6Zn_{23}Si$  ( $6 \times 4 + 23 \times 12 = 300$ ). However, this is not necessarily in contradiction to our previous rationalization, that the voids in the compounds with high zinc content might be needed to accommodate non-bonding electrons of the zinc atoms [1,2], since the silicon atoms in  $Zr_6Zn_{23}Si$  occupy voids formed by the zirconium atoms. The fact that the binary  $Th_6Mn_{23}$ -type lanthanoid manganese and iron compounds  $La_6Mn_{23}$  and  $La_6Fe_{23}$  can take up large amounts of hydrogen (Table 4) shows that the interstitial sites, formed mainly by the transition metal atoms with relatively low electron count, can accommodate additional valence electrons (from the hydrogen atoms). We doubt that  $Y_6Zn_{23}$  [25] or  $Zr_6Zn_{23}Si$  could take up as much hydrogen as is present in  $Y_6Mn_{23}H_{23}$  [17].

#### Acknowledgements

We thank Dipl. Ing. U. Rodewald for the collection of the single-crystal intensity data and Mr. K. Wagner for the work at the scanning electron microscope. We appreciate a generous gift of silica tubes by Dr. G. Höfer of the Heraeus Quarzschmelze. We also thank the Alexander von Humboldt Foundation for a stipend to one of us (X.C.). This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der chemischen Industrie.

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