priori vorausgesetzt, so würde die von Nowotny *et al.* (1968) seinerzeit vorgeschlagene Strukturformel recht naheliegend erscheinen. Die Schwingungsspektren der OH/OD-Gruppen des Ge(2)-Tetraeders fallen wahrscheinlich mit den breiten Banden der Wassermoleküle zusammen. Die Banden der Deformationsschwingungen der Wassermoleküle sind zu schwach und zu breit, um eine Aussage über die Anzahl der verschiedenartigen Wassermoleküle zu gestatten. Die Deformationsschwingungen der OH/OD-Gruppen wurden nicht beobachtet.

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The Th_2Zn_{17} Structure: Accounting for the Constant Axial Ratio of the Hexagonal Cell

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Abstract

The dimensional behaviour of phases with the Th_2Zn_{17} (M_2N_{17}) structure is analysed in order to account for the extreme constancy of the rhombohedral angle, or axial ratio of the equivalent hexagonal cell ($c/a = 1{\cdot}46 \pm 0{\cdot}01$). Both cell edges a and c vary linearly with D_M (D = diameter) at constant D_N and with D_N at constant D_M, and the variation of both a and c with D_M is identical. These conditions uniquely identify the slightly rumpled hexagon-diamond-triangle nets of M and N(3) atoms about (0001) planes at $z = 0$, $\frac{1}{3}$ and $\frac{2}{3}$ as controlling the a parameter and the

$$-N(1)-\underbrace{M-N(4)-M}_{\text{(cage)}}-N(1)-$$

lines of atoms along [0001] as controlling the c parameter, the M—N(4)—M cage length depending only on D_N. Not only do the equations derived for the variation of a and of c with D_M and D_N allow the accurate calculation of the unit-cell dimensions, but they are shown to lead to the constant axial ratios that are found for the phases.

Introduction

One of the most fascinating metallic-alloy structures is the Th_2Zn_{17} type (rhombohedral) because of the extreme constancy of the axial ratio of the equivalent hexagonal cell which varies by no more than $\pm 0{\cdot}008$ from $1{\cdot}460$ for 43 phases as pointed out by Johnson, Smith & Wood (1969) in their investigation of phases with this structure. Such invariance in the structure of a metallic alloy is indeed surprising, although it may be observed in nonmetallic alloys when it results from the rigidity of the hybrid sp^3 bond angle. For example the axial ratio of phases with the Na_3As structure (hexagonal) only varies by $\pm 0{\cdot}03$ from a value of $1{\cdot}79$ (with

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one possible exception) because of the pivotally resonating sp^3 bonds from As to its (6 + 2) Na neighbours (Pearson, 1972). Also the axial ratio in some 20 phases with the wurtzite structure (hexagonal) only varies between 1·595 and 1·658 about the ideal value of 1·633, in marked contrast to that of phases with the NiAs structure where it varies from about 1·2 to 2·0!

Although the axial ratio appears to be an invariant parameter of the Th_2Zn_{17} structure, it cannot be causally so, since it must result from the relative constancy of interatomic distances in the directions of the unit-cell axes or of interatomic distances lying in directions at an angle to the unit-cell axes. It is the object of this paper to analyse the relationships between the atoms in the Th_2Zn_{17} structure and discover the reason for the constancy of the axial ratio, this being part of a programme to understand the ordering, stability and dimensional relationships in the crystal structures of alloys.

The Th_2Zn_{17} structure

There are 38 atoms in the hexagonal cell of the Th_2Zn_{17} (M_2N_{17}) structure. The M atoms occupy one site-set and the N atoms four site-sets. The coordination number (CN) of the N atoms is 12 to 14 and that of the M atoms is 20, although seven of the neighbours are at distances corresponding to fairly weak connections. CN 12 radii of Teatum, Gschneidner & Waber (1960) have therefore been used in the analyses of this paper. However, their values of 3·12 and 3·16 Å respectively for the diameters of U^{VI} and Pu^{V} clearly are inappropriate for the U_2Zn_{17} and Pu_2Zn_{17} phases. Values 3·55 and 3·48 Å respectively, close to those suggested by Zachariasen (1973) for U^{IV} and Pu^{IV}, lead to sensible agreement between the behaviour of these phases and others with the Th_2Zn_{17} structure. The constancy of the axial ratio is even more surprising when it is seen that phases with the structure have M atoms with diameters (D_M) between approximately 2·9 and 4·5 Å, N atoms with diameters (D_N) between 2·25 and 3·20 Å and diameter ratios D_M/D_N lying between 1·24 and 1·46.

Accurate atomic parameters have been determined for six phases with the structure type, five reviewed by Johnson *et al.* (1969) and Ba_2Mg_{17} determined by Kanda & Carter (1973). Typical interatomic distances are given for Pr_2Fe_{17} by Johnson, Wood, Smith & Ray (1968). A number of these are closer than the appropriate radii sums and as an *a priori* assumption, it might be expected that arrays of atoms connected closely together would be responsible for controlling the unit-cell dimensions. Prominent among such arrays in the Th_2Zn_{17} structure are: (i) the slightly rumpled hexagon-diamond-triangle array of M and $N(3)$ atoms about (0001) planes at $z = 0, \frac{1}{3}, \frac{2}{3}$. (ii) The slightly rumpled Kagomé nets of $N(2)$ and $N(4)$ atoms about (0001) planes at $z = \frac{1}{6}, \frac{1}{2}$ and $\frac{5}{6}$. (iii) The off-set chains of triangles of $N(2)$ and $N(3)$ atoms lying approximately in planes whose trace is in the [0001] direction. These triangles also connect to the hexagons of $N(3)$ atoms at $z = 0, \frac{1}{3}$ and $\frac{2}{3}$, giving what might be described as a three-dimensional 'sheared' Kagomé net. (iv) There are also lines of M–$N(1)$–$N(1)$–M atoms lying along [0001] directions with the M atoms at the end of the lines being connected through a cage of six $N(4)$ atoms. These are shown in Fig. 1.

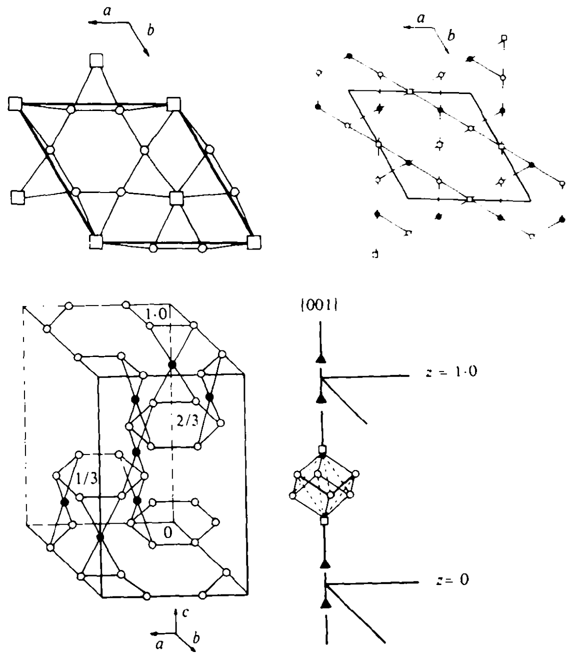

Fig. 1. Th_2Zn_{17} structure: arrays of atoms corresponding to the description in the text. (i) Is the top left, (ii) top right, (iii) bottom left and (iv) bottom right.

If, for example, the (0001) $N(2)$ and $N(4)$ Kagomé net and the [0001] $N(2)$ and $N(3)$ chains control the unit-cell dimensions, then

$$a \simeq 2\sqrt{3}.D_N, \quad c \simeq 3\sqrt{3}.D_N \quad \text{and} \quad c/a \simeq 1{\cdot}50,$$

but I made little progress with such relationships. Furthermore, the diameter ratio D_M/D_N, usually a good parameter to pursue, appeared particularly unprofitable! Instead, analysis of the dependence of the a and c parameters of the unit cell on the diameters of the component atoms shows uniquely which interatomic contacts control the unit-cell dimensions.

Determination of the interatomic contacts controlling the unit-cell dimensions

Figs. 2 and 3 show that both a and c vary linearly with D_N at constant D_M, and with D_M at constant D_N. From these figures the following equations for the variation of a and c are derived:

$$a + (3{\cdot}203 - D_N)2{\cdot}286 = 10{\cdot}0 - (3{\cdot}575 - D_M) \times 0{\cdot}727,$$
$$c + (3{\cdot}227 - D_N)3{\cdot}846 = 15{\cdot}0 - (3{\cdot}575 - D_M) \times 0{\cdot}727,$$

whence

$$a = 2{\cdot}286D_N + 0{\cdot}727D_M + 0{\cdot}079, \qquad (1)$$
$$c = 3{\cdot}846D_N + 0{\cdot}727D_M - 0{\cdot}010, \qquad (2)$$

and

$$c - a = 1{\cdot}560D_N - 0{\cdot}089. \qquad (3)$$

The surprising feature of these equations is that both cell axes vary identically with the diameter of the M atom. This limits control by M atoms to the $\langle 10\bar{1}0\rangle$ and [0001] directions (*i.e.* along the cell axes) and excludes such chains of atoms as M—N(4)—M—N(4)—M—N(4) which runs in the $[\bar{1}101]$ direction parallel to the long body diagonal of the hexagonal cell.

In the (0001) plane the only possibility of satisfying equation (1) is with the net shown in Fig. 1(i), so that $a \simeq D_M + 2D_N$. (In fact, the 40 binary phases essentially realize this relationship with $D_M + 2D_N = 1{\cdot}04a - 0{\cdot}18$.) Thus a depends on a single value of D_M and so c must also depend on a single value of D_M. The M—N(1)—N(1)—M lines of atoms along [0001] with length $D_M + 2D_N$ provide the only possibility of realizing this. However the M atoms at the end of these chains are linked by a cage of six N(4) atoms (Fig. 1), so that

$$c \simeq D_M + 2D_N + (M\text{—}M \text{ distance})$$

and since $a \simeq D_M + 2D_N$,

$$c - a \simeq (M\text{—}M \text{ distance}),$$

whereas equation (3) above gives $c - a = 1{\cdot}560D_N - 0{\cdot}089$.

Therefore the length of the M—N(4)—M cage along [0001], although involving the diameter of the M atom, must be largely independent of it and depends only on D_N. This requirement appears to be satisfied; the M—M distance varies linearly with D_N and somewhat randomly with D_M for the six phases whose atomic parameters have been determined accurately. The observed

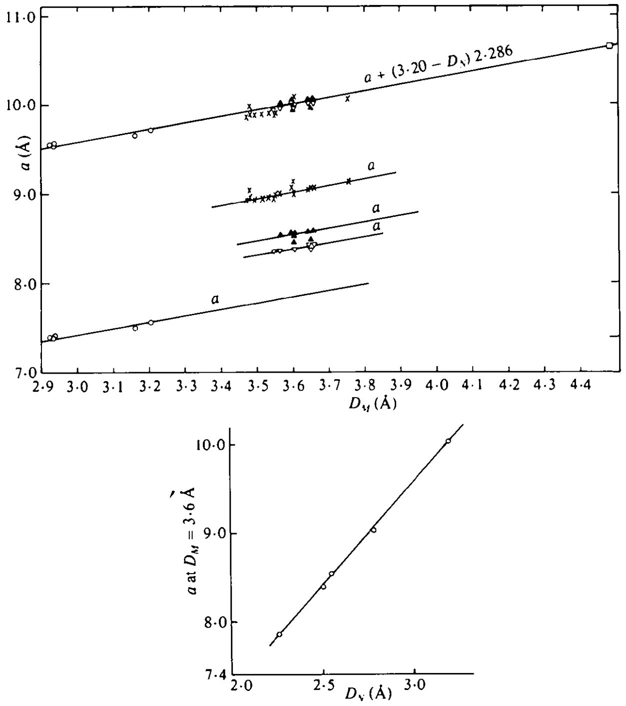

Fig. 2. Plots showing (i) unit-cell edge a *versus* D_M for M_2N_{17} phases with N = Be (○), Co (▽), Fe (▲), Zn (x) and Mg (□), (ii) a at D_M = 3·6 Å *versus* D_N for the five N components, Be, Co, Fe, Zn and Mg, and (iii) a + (3·20 − D_N) 2·286 *versus* D_M for all 40 binary phases with the Th_2Zn_{17} structure.

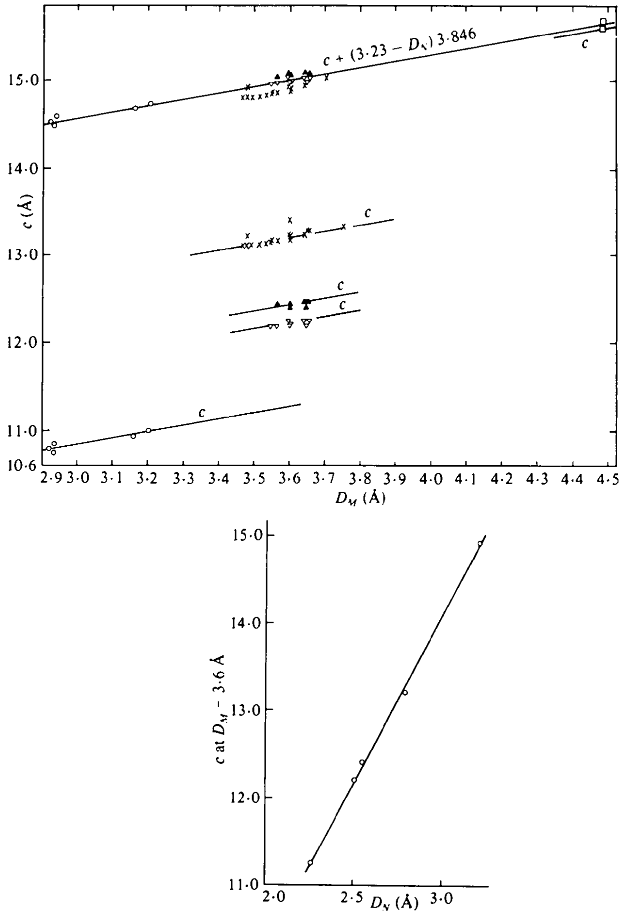

Fig. 3. Plots showing (i) unit-cell edge c *versus* D_M for M_2N_{17} phases with N = Be (○), Co (▽), Fe (▲), Zn (×) and Mg (□), (ii) c at D_M = 3·6 Å *versus* D_N for the five N components, Be, Co, Fe, Zn and Mg, and (iii) c + (3·23 − D_N) 3·846 *versus* D_M for all 40 binary phases with the Th_2Zn_{17} structure.

M–M distance also varies linearly with the observed $(c - a)$ values. The dependence of the observed *M–M* distance on D_N can be represented by the equation: (*M–M* distance) $= 1{\cdot}58D_N - 0{\cdot}103$, not significantly different from equation (3) obtained from the cell edges of 40 binary phases with the structure. In the *M–N*(4)*–M* cages each *M* atom is joined to three *N*(4) atoms at a distance equal to the radii sum $(R_M + R_N)$ and to the other three at a somewhat longer distance. The *N*(4)*–N*(4) distances are closer than the CN 12 diameter of the *N* atoms. Since the *N*(4) atoms have freedom in the (0001) plane (*x* parameter) and in the [0001] direction (*z* parameter), and the *M* atoms have freedom along [0001] (*z* parameter), it is not inconceivable that the cage length (*M–M* distance) could be largely independent of the *M* atom diameter (see Appendix).

Hence the atomic arrays controlling the unit-cell dimensions are uniquely identified. They are the (0001) rumpled *M* and *N*(3) hexagon-diamond-triangle nets which control *a* and the [0001] lines of atoms

$$N(1)\text{–}N(1)\text{–}\underbrace{M\text{–}N(4)\text{–}M}_{\text{cage}}\text{–}N(1)\text{–}N(1)$$

which control *c*, the *M–N*(4)*–M* cage length being controlled by the diameter of the *N* atoms.

Constancy of the axial ratio

Equations (1) and (2) clearly do not give a mathematically constant *c*/*a* ratio, yet this is achieved even though D_M increases by 53% and D_N by 42% on going from Ti_2Be_{17} to Ba_2Mg_{17}. Fig. 4 shows contours for $c/a = 1{\cdot}45$, $1{\cdot}46$ and $1{\cdot}47$ as a function of D_M and D_N, together with lines for $D_M/D_N = 1{\cdot}24$ and $1{\cdot}46$, the limits of the diameter ratio for phases presently known to have the structure. It also shows the positions of phases currently known to take the structure. The average observed axial ratio of phases formed by Zn is indeed larger than that of phases formed by Fe and by Co as the diagram would indicate. Clearly there is a strong correlation of the constant axial ratio and the diameter ratio and the former varies very slowly with changing diameter ratio.

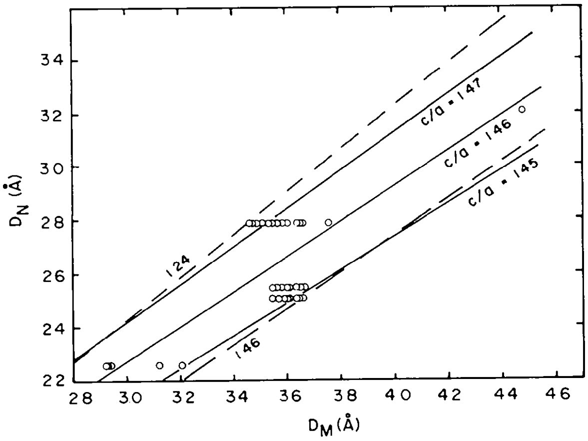

Fig. 4. Contours for axial ratios $c/a = 1{\cdot}45$, $1{\cdot}46$ and $1{\cdot}47$ as a function of D_M and D_N (full lines) and constant diameter ratios $D_M/D_N = 1{\cdot}24$ and $1{\cdot}46$ (broken lines). Also shown are phases having the Th_2Zn_{17} structure (○).

Discussion

The radius ratio, R_M/R_N, is generally taken as the basis of attempts to analyse geometrical relationships in the structures of metallic phases. But this introduces unsolved difficulties regarding atomic coordination and the appropriate atomic radius to use. This is especially so when one component has several different coordination numbers in the structure, or when the distances from the central atom to its neighbours forming the convex coordination polyhedron are very disparate. The method of analysing the unit-cell dimensions of phases with the Th_2Zn_{17} structure in terms of the CN 12 diameters of the component atoms (D_M and D_N) used in this paper avoids all of these difficulties, since change of coordination from CN 12 only subtracts or adds a constant value to the diameters. Therefore the equations derived are independent of the coordination of the atoms concerned, except for a constant term. Furthermore, the form of the equations, expressed directly in terms of D_M and D_N, rather than ratios, is very suitable for making deductions regarding the atomic arrays which control the structural dimensions.

In the present paper, not only are the features controlling the unit-cell dimensions and therefore the very constant value of the axial ratio uniquely identified, but it is clear from equations (1) and (2), that the unit-cell dimensions of any new phase that might take the Th_2Zn_{17} structure can be calculated very precisely from knowledge of D_M and D_N. Thus the calculated *a* and *c* values are respectively within an average of $|0{\cdot}030|$ and $|0{\cdot}027|$ Å of the observed values for 19 phases with $N =$ Be, Mg, Fe and Co (excluding the $M =$ Y and Ce phases whose exact valences and therefore diameters are unknown), so they are correct to within a fraction of a per cent. Both the calculated *a* and *c* values of the Zn compounds are somewhat too high, indicating that the assumed Zn diameter of 2·788 Å is too large. A diameter of 2·760 Å gives average agreement of $|0{\cdot}012|$ for *a* and $|0{\cdot}022|$ Å for *c* for 12 M_2Zn_{17} phases (those whose *M* atom valencies and diameters are known with certainty).

It is interesting to note that the *N*(2) atoms which have no variable parameters are not involved in the atomic arrays that control the unit-cell dimensions, and secondly that the variable parameters of the other atoms all operate in the direction of their neighbours which are part of an atomic array controlling the unit-cell dimensions, as summarized below:

M: z: M–N(1) distance along [0001]

N(1): z: N(1)–N(1) and M–N(1) distances along [0001]

N(3): x: N(3)–N(3) and M–N(3) distances approximately along $[10\bar{1}0]$, $[01\bar{1}0]$

N(4): x,z: N(4)–N(4) and M–N(4) distances in M–N(4)–M cage.

Clearly it is this feature which permits the structure to maintain a constant axial ratio despite the considerable variation of the sizes of the atoms in different phases, since major relative adjustments of the atom positions can occur without influencing the cell dimensions in the way that would be required if the atomic parameters concerned had fixed values.

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APPENDIX

An essential argument of the paper is that the [0001] M–M distance should be independent of D_M for phases with the same N atom. Unfortunately only two of the six phases whose atomic parameters are accurately determined have the same N component, but the M–M distance is identical to within 0·02 Å for them. Nevertheless, the relationship (M–M distance) = $1{\cdot}58\ D_N - 0{\cdot}103$ can be used to correct for the different sizes of the N atoms. The table below shows that the M–M distances so adjusted for a constant D_N value of 2·8 Å are indeed very constant over a variation of D_M from 2·9 to 4·5 Å.

Phase	M–M distance (Å)	D_M (Å)
Nb_2Be_{17}	4·327	2·936
U_2Zn_{17}	4·309	3·55
Th_2Fe_{17}	4·318	3·596
Th_2Co_{17}	4·313	3·596
Pr_2Fe_{17}	4·297	3·656
Ba_2Mg_{17}	4·387	4·486.

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La Structure Cristalline du Fluorotitanate de Potassium $KTiF_4$

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Abstract

The crystal structure of $KTiF_4$, $M_r = 162{\cdot}99$, has been determined from X-ray diffraction data measured on an automatic diffractometer. The compound crystallizes in the orthorhombic system, space group *Pcmn* (*Pnma*) with eight molecules per unit cell. The lattice constants are $a = 7{\cdot}944$ (10), $b = 7{\cdot}750$ (10), $c = 12{\cdot}195$ (8) Å, $D_m = 2{\cdot}85$ (5), $D_c = 2{\cdot}88$ Mg m^{-3}, $Z = 8$. Least-squares refinement of coordinates and anisotropic

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