Unfortunately, however, nothing is known about the species existing in the vapour phase from which the crystals investigated in these two papers were grown. So it may be possible that the growth species has the formula unit $MoO_2Cl_2.H_2O$. This is supported by the further result that the compound can be sublimed in a tube moved back and forth in a stream of HCl gas (Schröder, 1969). Thus it evaporates congruently and when the crystals of $MoO_2Cl_2.H_2O$ grow again, the 'components', MoO_2Cl_2 and H_2O, should be almost exactly in a 1:1 ratio, and thus the formula unit $MoO_2Cl_2.H_2O$ can at least be regarded as the quasi growing species.

The method of preparation of Schröder & Nørlund Christensen (1972) supplies most of the crystalline material as a semicrystalline product (Schröder, 1969). This can be understood if it is assumed that every product of crystallization of $MoO_2Cl_2.H_2O$ is a result of the possibilities of orientation in which this formula unit can be placed. These possibilities could be described as a rotational degree of freedom with adjustment in two positions of the described polyhedra of structures A and $\bar{A}$.

It was found by Schröder & Nørlund Christensen (1972), that at 155 °C structure B is irreversibly transformed into structure A (and $\bar{A}$). This may take place by a mere rotation of some polyhedra within the unit cell of structure B. As a consequence, it has to be concluded that the two positions of the water molecule are also equal in their site energy and only the 'longer-range order' between two polyhedra within the chains corresponds to a somewhat higher energy in structure B than in structures A and $\bar{A}$.

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The Effect of Fast-Neutron Irradiation on Zr₄Al₃

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The effect of fast-neutron radiation on the structure of Zr_4Al_3 has been studied using X-ray diffractometry. The changes in line intensity are explained by the disordering caused by the replacement of 0·5 atom in zirconium sites by aluminum. The anisotropic changes in the size of the unit cell can be partially explained by the geometrical changes produced by the disordering of atoms of unequal size.

Introduction

The effect of fast-neutron irradiation on the structure of the intermetallic alloy having the composition Zr_4Al_3 has been investigated using X-ray powder diffraction methods. The aim of the study was to compare the effects of fast-neutron irradiation in this alloy with those produced in the binary σ phases already investigated by similar techniques (Wilson & Parselle, 1965; Spooner, 1968). A characteristic feature of the structure of the σ-phase alloy and Zr_4Al_3 is the vertical row of transition-metal atoms whose separation is much less than that normally encountered in intermetallic structures. It was hoped that a comparison of the damage in both structures would lead to a better understanding of the importance of these atoms in their respective structures.

Experimental

Samples of Zr_4Al_3 powder were irradiated in aluminum capsules in the HIFAR reactor at A.E.E.C., Lucas Heights, New South Wales, to nominal doses of 10^{19} and 10^{20} fast neutrons (> 1 MeV) at the operating temperature of the reactor (~ 60 °C). The Debye–Scherrer powder films taken of the specimens before and after irradiation were used mainly for reference purposes. Measurements of lattice parameters and line intensities were made on diffractometer traces, all taken at the same speed and with a fairly long time constant. Reproducibility was good and average values of 2θ readings were taken from three charts run under similar conditions. Lattice parameters for the irradiated

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specimens were calculated using the least-squares technique for hexagonal structures outlined by Klug & Alexander (1954). The relative intensities of all specimens were obtained by using a planimeter to measure the areas under lines on the diffractometer traces. The uncorrected integral line breadths defined by $B = \int Idl/I_{max}$ were measured for some low-angle lines.

Results

The measured lattice parameters and the fractional changes in a and c for the unirradiated and irradiated specimens are given in Table 1.

The relative intensities of the diffraction lines of the unirradiated specimens were calculated for the ordered Zr_4Al_3 structure published by Wilson, Thomas & Spooner (1960) and these are shown in Table 2 in the column headed Calc. 1(a). All intensities given in this Table are normalized with respect to totals of observed and calculated values. The relative intensities shown in the column headed Calc. 1(b) are calculated values assuming the limited disorder which is used in explaining the observed line intensities of the high-dose-irradiated specimen discussed later. The agreement between observed and calculated intensity values using the ordered Zr_4Al_3 structure is good.

Discussion

Disorder produced by neutron irradiation

It was apparent from the powder photographs of the irradiated samples that the low-index lines 10.0 00.1 and 10.1 suffered abnormally large intensity changes, whilst the higher-angle lines were considerably broadened, especially in the specimen irradiated to 10^{20} nvt. The latter fact made the parameter determinations difficult and dependent on lines in the range $2\theta < 70°$, which precluded very high accuracy in the extrapolation of 2θ to $90°$.

The relative intensities of the low-angle reflexions are much more sensitive to changes in order than are the higher-angle reflexions, as in the case of the σ phase (Wilson & Parselle, 1965). The same interpretation of disorder was assumed and the extent of this disorder in the specimen irradiated to 10^{20} nvt was estimated by a trial-and-error method. The difference in scattering factors between Zr and Al, (atomic numbers 40 and 13 respectively), leads to the low-angle lines such as 00.1, 10.0, 10.1, 20.1, 20.2 etc., showing marked changes in relative intensity as a result of disorder.

For complete random order 10.0 and 10.1 give zero relative intensity, whilst 20.1 and 21.2 become very strong lines. By considering the changes in relative intensity caused by the systematic replacement of Zr by Al atoms it was possible to determine the ordering scheme which gave the best agreement between normalized observed and calculated relative intensities. The most satisfactory ordering scheme found was the one based on the 4 Zr sites being occupied by 3·5 Zr and 0·5 Al atoms per unit cell and the 3 Al sites being occupied by 2·5 Al and 0·5 Zr atoms per unit cell. The renormalized intensity calculations, for the ordered structure and the normalized calculations for the assumed disordered structure, are given in Table 2 in the columns headed Calc. 2(a) and Calc. 2(b) respectively.

The observed line intensities of the low-dose-irradiated specimen, seen in Table 2, are intermediate between those of the unirradiated and high-dose-irradiated specimens indicating some disorder. The normalized intensity values quoted in columns headed Calc. 3(a) and Calc. 3(b) refer to the original ordered structure and a structure possessing the disorder assumed for the high-dose-irradiated specimen respectively. These values support the explanation of very small disorder in this specimen.

The changes in the lattice parameters, seen in Table 1, are similar to those reported for the hexagonal ceramic materials such as BeO (Hickman, Sabine & Coyle, 1962) and MgO (Hickman & Walker, 1965), and are in contrast to those reported for σ phases, where $\Delta a/a$ is invariably negative and $\Delta c/c$ much larger and positive.

A sphere-packing model for the calculation of lattice parameters

If we accept the fact that the Zr_4Al_3 structure is a sphere-packing structure, as suggested by Frank & Kasper (1959), a change in order should lead to changes in lattice parameter dependent on the radii of the constituent elements. These changes can be calculated from the geometry of the structure.

The Zr_4Al_3 structure can be regarded as a close-packed hexagonal structure in which the basal layer consists of Al atoms containing vacant sites at $\frac{1}{2}\frac{1}{2}0$. A layer of Zr atoms in close-packed positions but containing vacancies at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ is stacked on the basal layer with the rows of Zr atoms at right angles to the rows of Al atoms, as shown in Fig. 1. The crystal cannot have the normal c.p.h. $ABA \ldots$ stacking sequence because the difference in radii of the atoms in the alter-

Table 1. *Lattice parameters of* Zr_4Al_3

Specimen	a (Å)	c (Å)	$\Delta a/a \times 10^4$	$\Delta c/c \times 10^4$	$(\Delta V/V) \times 10^4$
Unirradiated	$5\cdot4317 \pm 0\cdot0005$	$5\cdot3890 \pm 0\cdot0005$	–	–	$(V_0 = 25\cdot349 \text{ Å}^3)$
Irradiated (5×10^{19})	$5\cdot4333 \pm 0\cdot0005$	$5\cdot3945 \pm 0\cdot0008$	3	8	11·3
Irradiated (10^{20})	$5\cdot4532 \pm 0\cdot0008$	$5\cdot4602 \pm 0\cdot0008$	37	131	172

Table 2. Zr₄Al₃ – *Relative X-ray line intensities*

hkl	Unirradiated specimen				Irradiated specimen, high dose				Irradiated specimen, low dose			
	2θ(°)	Obs.	Calc. 1(a) (ordered)	Calc. 1(b) (disordered)	2θ(°)	Obs.	Calc. 2(a) (ordered)	Calc. 2(b) (disordered)	2θ(°)	Obs.	Calc. 2(b) (ordered)	Calc. 3(b) (disordered)
			Line intensity				Line intensity				Line intensity	
00·1	16·28 ($\bar\alpha$)	12	18	6	15·98 ($\bar\alpha$)	3·5	12	4	16·22 ($\bar\alpha$)	11	14	4
10·0	18·69 ($\bar\alpha$)	8·5	16	10	18·55 ($\bar\alpha$)	4·5	10	6	18·65 ($\bar\alpha$)	9	13	7
10·1	24·93 ($\bar\alpha$)	8	15	10	24·69 ($\bar\alpha$)	3·5	9	6	24·90 ($\bar\alpha$)	8	11	7
11·0, 00·2	32·80, 33·20 ($\bar\alpha$)	106	110	103	32·61, 32·95 ($\bar\alpha$)	66	70	67	32·76, 33·14 ($\bar\alpha$)	87	85	77
11·1	36·84 ($\bar\alpha$)	75	59	67	36·62 ($\bar\alpha$)	56	37	41	36·83 ($\bar\alpha$)	58	45	50
20·0, 10·2	38·30 ($\bar\alpha$)	143	129	147	37·82 ($\bar\alpha$)	98	82	91	38·24 ($\bar\alpha$)	122	99	109
20·1	41·72 ($\bar\alpha$)	21	27·5	43	41·44 ($\bar\alpha$)	17	17·5	27	41·67 ($\bar\alpha$)	18	21	32
20·2	51·38 ($\bar\alpha$)	21	21·5	13	50·93 ($\bar\alpha$)	10	14	8	51·32 ($\bar\alpha$)	16	17	9·5
30·0	58·70 (α_1)	16	18	17	58·42 ($\bar\alpha$)	10	12	10	58·61 (α_1)	12	14	13
30·1	61·40 (α_1)	30	24·5	28	61·10 ($\bar\alpha$)	20	16	17	61·33 (α_1)	20	19	21
11·3	61·67 (α_1)	50	48	53	61·91 ($\bar\alpha$)	32	31	33	61·64 (α_1)	34	37	39
21·2	62·37 (α_1)	9	7	11		7	4	7	62·33 (α_1)	8	5	8
20·3	65·15 (α_1)	28	27	32	64·46 ($\bar\alpha$)	17	17	20	65·09 (α_1)	18	21	24
22·0, 00·4	68·98, 69·58 (α_1)	18	16	16	68·68, — ($\bar\alpha$)	10	10	10	68·94, 69·48 (α_1)	13	12	12
22·2, 11·4	79·18 (α_1)	31	29	33	79·18 ($\bar\alpha$)	18	19	20	79·06 (α_1)	22	23	25
30·3, 31·2	81·86, 82·12 (α_1)	16	21	19	81·31 ($\bar\alpha$)	11	13	12	81·16, 81·65 (α_1)	14	16	14
41·0, 30·4, 41·1, 11·5	97·13, 97·72, 99·53, 100·41 (α_1)	26	27	31	96·70, 99·75 ($\bar\alpha$)	14	18	19	97·08, 97·58, 99·38, 100·33 (α_1)	19	21	24
32·2, 20·5, 40·3	103·10 (α_1)	4	5	7	—	—	3	4	—	—	2	5

nate layers ($r_{Al}=1\cdot40$ Å, $r_{Zr}=1\cdot60$ Å) prevents a B layer of Zr atoms lying exactly above the appropriate B hollows of a close-packed Al layer without overlap. The form of stacking adopted allows the layer of Zr atoms in type I positions ($z=\frac{1}{2}$) to lie in the hollows formed by the triangles of Al atoms with adjacent Zr atoms in B and C hollows. This is equivalent to stacking a close-packed layer of Zr atoms at right angles to the close-packed Al layer. The packing difficulties which ensue when complete close-packed layers adopt this form of stacking are avoided by creating vacant sites in the Al layer and filling this space with *two* Zr atoms at $z=\frac{1}{4}$ and $z=\frac{3}{4}$. These ZrII atoms are compressed to form oblate spheroids, a feature which is characteristic of transition-metal atoms occupying this kind of site. The coordination associated with the ZrII atoms is similar to that possessed by transition-metal atoms in the E sites of the σ-phase structure (Frank & Kasper, 1959). Thus, Zr_4Al_3 can be created by stacking incomplete close-packed layers of Al and ZrI atoms at right angles and threading these with rows of ZrII atoms. In accommodating the symmetrically compressed ZrII atoms, the Al and ZrI layers are forced

apart, and, assuming the atoms in these layers still remain in contact, the Al and ZrI atoms are strained symmetrically so that they become prolate spheroids.

The stacking of close-packed layers of unequal atoms yields a hexagonal unit cell whose c parameter can be determined from geometrical considerations. The atoms marked P, Q, R and S in Fig. 1, lie in vertical panels similar to that shown in Fig. 2(a). Six panels of this kind form hexagonal prisms around each pair of ZrII atoms in the unit cell. Supposing all the atoms in the panels are spheres prior to putting the ZrII atoms in position, the height of the unit cell is given by:

$$c_1=2\sqrt{(r_{Zr}+r_{Al})^2-r_{Zr}^2}\,.$$

Using the Goldschmidt radii $r_{Zr}=1\cdot60$ Å and $r_{Al}=1\cdot40$ Å, gives $c_1=5\cdot0754$ Å. The ZrII atoms are also spheres in contact prior to being forced into their positions in the structure, and, since there are two ZrII atoms in each unit cell, the value of the c parameter can be derived from:

$$c_2=4r_{Zr}\,,$$

assuming no distortion of the atoms. Putting $r_{Zr}=1\cdot60$ Å, gives

$$c_2=6\cdot40\text{ Å}\,.$$

In creating the structure c_1 is increased and c_2 decreased and the final value of the c parameter is given by a weighted mean of c_1 and c_2. In determining the nature of the averaging process it is borne in mind that there are, on the average, three panels per unit cell associated with one pair of ZrII atoms, so that the change expected in c_1 will be one third that found in c_2 when the two elements of the structure are put together. Thus, we take the unirradiated c parameter to be given by:

$$c_0=\frac{3c_1+c_2}{4}\,.$$

Using the calculated values of c_1 and c_2:

$$c_0=5\cdot4066\text{ Å}\,.$$

This calculated value for c compares very favourably with the observed value of c for the unirradiated crystal, *viz.* $c_0=5\cdot3890$ Å.

It is more difficult to obtain an estimate of the a parameter because the natural elements of structure that might be used for determining a in the alternate layers of Al and ZrI atoms, are periodically interrupted by the vertical rows of ZrII atoms. In order to obtain a reasonable value for a we first consider the fundamental structural motif formed by three Al atoms (marked A in Fig. 1) and one ZrI atom (marked B in Fig. 1). These four atoms form a tetrahedral unit, the side of the triangular base of Al atoms being half the size of the hexagonal unit cell of the planar aluminum lattice a_1, *i.e.*

$$a_1/2=2\,.\,r_{Al}\,.$$

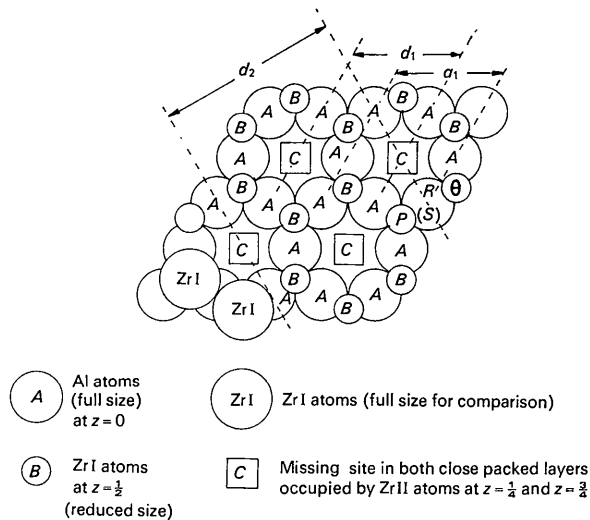When the structural motifs are joined together all the

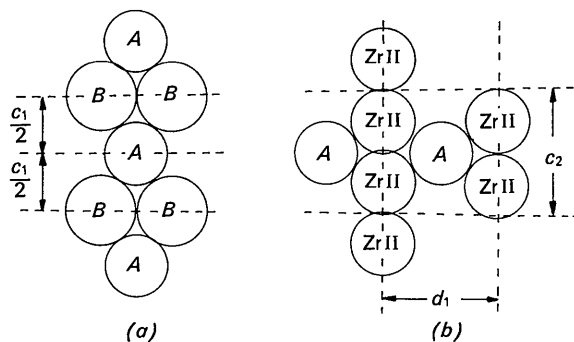Fig. 1. Packing in Zr_4Al_3.

(a) *(b)*

Fig. 2. Alternative ways of packing to give different estimates of c.

ZrI atoms lie on a parallel two-dimensional hexagonal lattice of side a_2, where:

$$a_2/2 = 2r_{Zr} \cos 30°.$$

In creating the structure of Zr_4Al_3 three such tetrahedral motifs come together to form a symmetrical planar unit with one Al atom from each motif becoming a member of the fourth central tetrahedral unit that is formed. This larger structural unit provides three of the vertical planes of Al and ZrI atoms that form the tubes surrounding the ZrII atoms. These vertical planes were used as a basic building unit for the estimation of the c parameter. By the addition of more tetrahedra with bridging ZrI atoms the complete Zr_4Al_3 structure can be built up. The Al base of the tetrahedra and the ZrI–ZrI links between them form the basic building units in the horizontal planes, and, if there were no ZrII atoms to bind the tetrahedra closer together, the average of the two quantities a_1 and a_2 would be a reasonable estimate of the hexagonal lattice created.

In order to take into account the effect of the ZrII atoms, we assume that in binding the three tetrahedral units together to form the larger unit of structure, two adjacent rows of ZrII atoms form a vertical plane containing a structural unit of ZrII and Al atoms in contact, Fig. 2(b). The horizontal distance between the vertical rows of ZrII atoms assuming spheres in contact, is given by:

$$d_1 = 2\sqrt{(r_{Al} + r_{Zr})^2 - r_{Zr}^2} .$$

In the final Zr_4Al_3 structure this distance becomes equal to the shorter diagonal of the hexagonal unit cell whose length is a. The ZrII atoms are also assumed to be in close contact with the ZrI atoms in the adjacent tetrahedra of the large structural units. The vertical planes containing these connexions also include Al atoms. Assuming close contact between spheres, the horizontal distance between two ZrII atoms (see Fig. 1) in these planes is given by

$$d_2 = 2(r_{Zr} + \sqrt{3}r_{Zr}) .$$

In the final structure this distance becomes equal to the longer diagonal of the unit cell whose length is $\sqrt{3}a$. We regard the average of d_1 and $d_2/\sqrt{3}$, viz. $a_3 = \frac{1}{2}(d_1 + d_2/\sqrt{3})$ as the size of the unit cell which could be derived from the ZrII connexions with the fundamental structural units. The average quantity $a_0 = \frac{1}{3}(a_1 + a_2 + a_3)$ is then taken as a reasonable estimate of the size of the Zr_4Al_3 unit cell which is ultimately formed by the various atoms being strained to give maximum packing efficiency.

Putting $r_{Al} = 1·40$ Å and $r_{Zr} = 1·60$ Å:

$$a_1 = 4r_{Al} = 5·6 \text{ Å}$$

and

$$a_2 = 4r_{Zr} \cos 30° = 2\sqrt{3} . r_{Zr} = 5·5426 \text{ Å} .$$

The similarity between these two values clearly favours the close-packing sequence chosen by these atoms in this structure. For calculating a_3:

$$d_1 = 2\sqrt{(r_{Al} + r_{Zr})^2 - r_{Zr}^2} = 5·0754 \text{ Å}$$

and

$$d_2/\sqrt{3} = \frac{2}{\sqrt{3}} (r_{Zr} + \sqrt{3}r_{Zr}) = 5·0475 \text{ Å}$$

whence

$$a_3 = \frac{1}{2}(d_1 + d_2/\sqrt{3}) = 5·0614 \text{ Å}$$

and

$$a_0 = \frac{1}{3}(a_1 + a_2 + a_3) = 5·401 \text{ Å} .$$

This estimate compares very favourably with the observed unirradiated value $a_0 = 5·4317$ Å, being less than 1 % in error.

Calculation of lattice-parameter changes

After neutron irradiation the atoms in each of the two layers and the vertical rows are no longer the same because of disordering. On the average one half atom of aluminum per unit cell is replaced by zirconium. Thus, the average radius of the atoms in the basal Al layer will be increased from r_{Al} to r'_{Al} where:

$$r'_{Al} = \frac{1}{6} (5r_{Al} + r_{Zr}) = 1·433 \text{ Å} .$$

Since there are only 2 Zr atoms per unit cell in the ZrI layer, the disordering gives rise to an average replacement of one quarter ZrI atom per unit cell and the average radius of the ZrI atoms becomes:

$$r'_{Zr} = \frac{1}{8} (7r_{Zr} + r_{Al}) = 1·575 \text{ Å} .$$

Likewise, the average radius of the ZrII atoms per unit cell becomes $r'_{Zr} = 1·575$ Å. Using the same calculation as for the unirradiated cell, the value of c_1 becomes:

$$c'_1 = 2\sqrt{(r'_{Zr} + r'_{Al})^2 - r'^2_{Zr}} = 5·1261 \text{ Å}$$

and

$$c'_2 = 4r'_{Zr} = 6·3 \text{ Å} ,$$

whence, the c_0 parameter of the irradiated cell will be given by:

$$c'_0 = \frac{1}{4} (3c'_1 + c'_2) = 5·420 \text{ Å} .$$

Using $r'_{Al} = 1·433$ Å and $r'_{Zr} = 1·575$ Å in the formulae developed earlier leads to the following values for the disordered structure:

$$a'_1 = 4r'_{Al} = 5·7332 \text{ Å}$$

$$a'_2 = 2\sqrt{3} \, r'_{Zr} = 5·4560 \text{ Å}$$

$$d'_1 = 2\sqrt{(r'_{Al} + r'_{Zr})^2 - r'^2_{Zr}} = 5·1261 \text{ Å}$$

$$d'_2/\sqrt{3} = \frac{2}{\sqrt{3}} (r'_{Zr} + \sqrt{3} \, r'_{Zr}) = 4·9687 \text{ Å}$$

$$a'_3 = \frac{1}{2} (d'_1 + d'_2/\sqrt{3}) = 5·0474 \text{ Å}$$

and

$$a'_0 = \frac{1}{3} (a'_1 + a'_2 + a'_3) = 5·4122 \text{ Å} .$$

From these results it follows that the effect of disordering is to increase the a and c parameters by

0·0109 and 0·0130 Å respectively. The calculated fractional changes are given by: $\Delta a/a = 20 \times 10^{-4}$ and $\Delta c/c = 24 \times 10^{-4}$ whilst the corresponding observed values are $\Delta a/a = 37 \times 10^{-4}$ and $\Delta c/c = 131 \times 10^{-4}$.

Conclusions

Bearing in mind the approximate nature of the calculations, the disordering can be regarded as giving a reasonably satisfactory account of the change in the *a* parameter, but, in order to account for the much larger change in *c* an additional effect must be invoked which gives rise to anisotropic expansion in a direction perpendicular to the basal layers. Owing to the layer-like nature of the structure it is expected that the point defects created by the fast-neutron bombardment would aggregate in these layers and give rise to preferential expansion of the lattice in the **c** direction. (A similar idea was postulated to account for the effects seen in irradiated σ; Spooner, 1968). It was hoped that a correlation might be observed in the changes of the measured diffractometer line breadths to support this contention but no such correlation could be observed. This was probably the result of inaccuracy associated with the relatively crude measurements. It would be conjectural to comment further on the precise nature of the point defects which remain in the structure after irradiation without more experimental evidence.

It is interesting to compare the extent to which the structural changes in Zr_4Al_3 and the σ phases can be ascribed to disordering. It is shown in another publication (Wilson & Spooner, 1973) that calculations very similar to those above can be used to estimate the sizes of the ordered and disordered unit cells of binary σ phases. These calculations lead to an increase in the *c* parameter and a very much smaller change, which is usually negative, in the *a* parameter of the tetragonal unit cell. The inclusion of a factor reflecting the importance of the vertical rows of compressed atoms (ZrII in Zr_4Al_3 and *E*-type atoms in σ phases) in both structures is essential to the successful prediction of the sizes of the unit cells and the signs of the changes involved on disordering. In both sets of calculations the changes produced by disordering are less than the observed changes produced by neutron irradiation but this can be explained, as above, by the effect of defect aggregates on lattice parameters. The calculations highlight the essential difference between the two structures, *viz.* the homogeneous nature of the atoms in the horizontal layers of Zr_4Al_3 and the marked heterogeneity of the layer atoms in the σ phase. The heterogeneous packing of atoms of such different radii as r_{Zr} and r_{Al} in the layers of the Zr_4Al_3 structure would lead to such undesirable voids and overlaps that the structure would be untenable and an alternative structure, such as a σ phase, would be more stable.

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