Short Communications

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A comparison of the structures Zr_2Al_3 and $ZrAl_2$.

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In the determination of the crystal structure of Zr_2Al_3 (Renouf & Beevers, 1961) it was stated that no simple relationship was obvious between this structure and $ZrAl_2$ (Wilson, 1959), from which it is formed peritectically. It may however be possible to relate the two structures by a comparison of the following features.

A projection of Zr_2Al_3 down the *c* axis is shown in Fig. 1(*b*). The space group is *Fdd*2 with

$$a = 9{\cdot}601,\ b = 13{\cdot}906,\ c = 5{\cdot}574\ \text{Å}\ .$$

$ZrAl_2$ is hexagonal with

$$a = 5{\cdot}282,\ c = 8{\cdot}748\ \text{Å},\ c/a = 1{\cdot}656\ .$$

The space group is $P6_3/mmc$, the structure being a Laves phase of the C14, $MgZn_2$ type. For comparison however it is convenient to choose an orthohexagonal form with

$$a = 5{\cdot}282,\ b' = 2a\cos 30° = 9{\cdot}148,\ c = 8{\cdot}748\ \text{Å}$$

and to compare the projection of two of these cells down the *a* axis as shown in Fig. 2(*b*) with the projection of Zr_2Al_3.

An examination of the layers perpendicular to the *b* axis of Zr_2Al_3 reveals that the structure from the layer 1 to the layer 3 is similar to one of the sequence types found in the Laves phases (Frank & Kasper, 1959) and can be compared with the sequence 1′–3′ of $ZrAl_2$. Figs. 1(*a*) and 2(*a*) show the projection of these sequences on a plane parallel to the layers. It will be seen that the outer layers 1 and 3 differ from the kagomé layers 1′ and 3′ by the absence of aluminium atoms in sites defined by the direction of the *d* glide planes. The structure of Zr_2Al_3 from the layer 5 to the layer 7 is the same as that from 1 to 3, and is compared with 5′–7′.

Further the structure of Zr_2Al_3 from the layer 3 to the layer 5 and from 7 to 1, can be compared in a similar manner with the alternative sequence type found in the Laves phases, that is with the sequence 3′–5′ and 7′–1′ of $ZrAl_2$.

Thus $ZrAl_2$ can be described as the two Laves sequence types stacked alternately, two sequences being sufficient to furnish the repeat unit; and Zr_2Al_3 can be described as two similar sequence types also stacked alternately but staggered so that four sequences are required to produce the repeat unit. The two Laves sequence types 1′–3′ and 3′–5′ of $ZrAl_2$ are related by a mirror plane

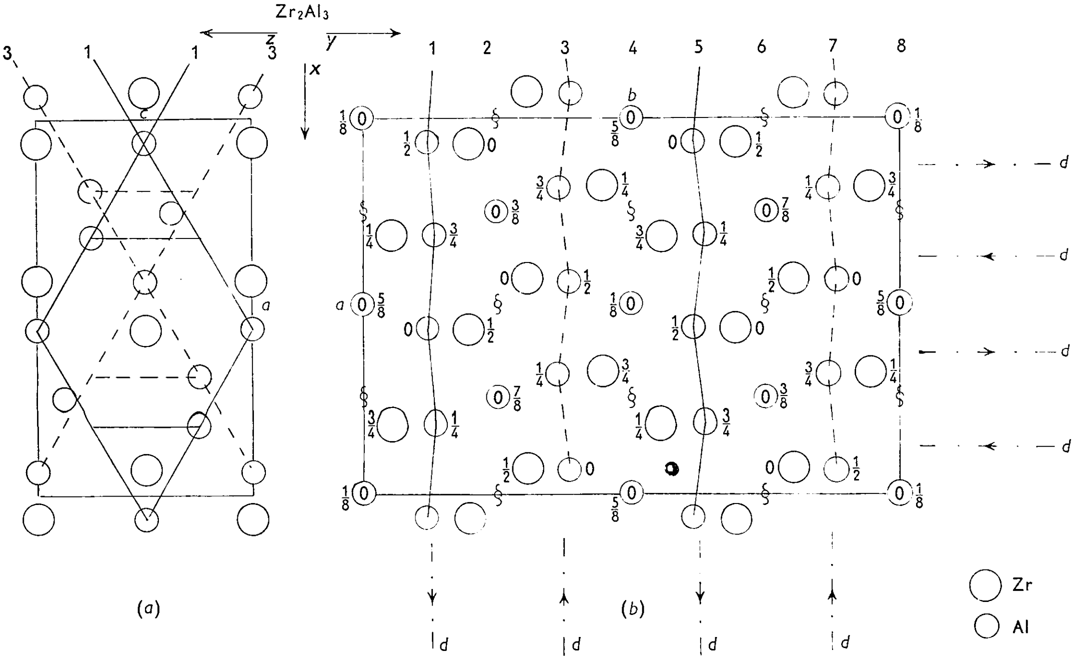

Fig. 1. (*a*) A projection of Zr_2Al_3 from the layer 1 to the layer 3 down the *y* axis. Al atoms lying in these layers are joined by the same type of line as used in (*b*). (*b*) A projection of Zr_2Al_3 down the *z* axis, giving the *z* co-ordinates of the atoms as fractions. Zr atoms are shown as large circles and Al atoms as smal circles.

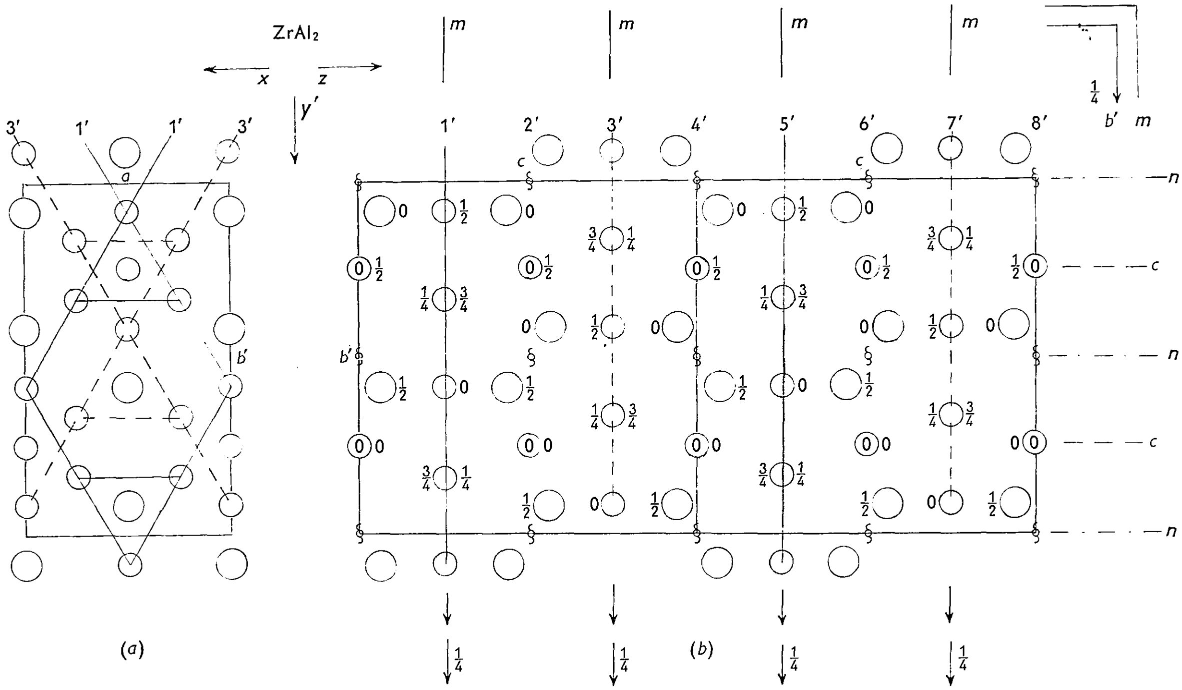

Fig. 2. (*a*) A projection of $ZrAl_2$ from the layer 1′ to the layer 3′ down the *z* axis. (*b*) A projection of $ZrAl_2$ down the *x* axis indicating the cell chosen for the comparison and giving the *x* co-ordinates of the atoms as fractions.

parallel to the layers at 3′, whereas in Zr_2Al_3 the sequences 1–3 and 3–5 are related by a *d* glide plane at 3. The relationship between 5′–7′ and 7′–1′ differs in this same way from that between 5–7 and 7–1. The repeat units 1′–5′ and 5′–1′ of $ZrAl_2$ are related by a mirror plane parallel to the layers at 5′ whereas in Zr_2Al_3 the units 1–5 and 5–1 are related by a *d* glide plane at 5.

It should be noted that in $ZrAl_2$ the hexagons of a kagomé net are centred by zirconium atoms from both sides. In Zr_2Al_3 the sequences are staggered so that one of these zirconium atoms is placed at the vacant site of the kagomé-type aluminium layer, thus producing a puckered triangular net. This might be taken to account for a relative contraction in the direction of stacking. From the figures other differences will be observed to be slight. The formulae are reconciled by noting the difference in the composition of the kagomé-type aluminium layers.

The two structures might therefore be considered as made up from sequences which are fundamentally similar, the main difference between them being the way in which the sequences are staggered.

References

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Some aspects of minimum-function diagrams.

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Presently the deconvolution of the Patterson function is attempted by the minimum function which is calculated by shifting the origin of the Patterson diagram by any interatomic vector $\mathbf{u}_{ab}$ and plotting the minima of the two values that superimpose. Though it is well known that the diagram gives the structure duplicated by its inverse about the midpoint of the shift-vector the symmetry of the diagram, $S(M)$, has not been completely investigated. We try to carry out this study here and indicate that $S(M)$ depends on the shift-vector and therefore can possibly lead to a method of distinguishing some of the Harker peaks from ghosts and some methods for solving centrosymmetric structures.

The theory is developed through an application of the matrix theory to the Patterson diagram (Buerger, 1950). In our discussion the set of N^2 interatomic vectors are represented as a square array $\mathbf{u}_{ij}$ where $\mathbf{u}_{ij}=\mathbf{r}_i-\mathbf{r}_j$, $\mathbf{r}_j$ being the atomic position-vector. The matrix $u_{ij}+u_{ab}$ implies shifting the Patterson by the vector $\mathbf{u}_{ab}$. We first consider the case where $\mathbf{u}_{ab}$ is a general vector, i.e. atoms