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A shift-lattice description of some face centred cubic alloy superstructures

Part 2.—Two-dimensional structures†

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The structures of the experimentally prepared binary alloys $Au_{31}Mn_9$ (two forms), $Au_{72}Mn_{21}$, $Au_{95}Mn_{28}$, $Au_{27}Mn_8$, $Au_{167}Mn_{49}$ and Au_3Mn (one form), have been analysed and found to be two-dimensional shift-lattices. It is shown that both the Au and Mn atom arrays lie upon separate but complementary shift-lattices. The known structures form only a small part of an infinite family of commensurate and incommensurate structures which can be constructed by smoothly varying the shift-lattice parameters applicable to the known phases. The two-dimensional shift-lattice structures described here are shown to be constructed from fragments of simpler one-dimensional shift-lattices analysed previously.

Introduction

In several recent papers we have used the shift-lattice formalism to describe a number of previously unrecognised structural relationships between different alloys.[1] In particular, the rather complex structures of a variety of alloys in the Au–Mn system with compositions between Au_4Mn and Au_3Mn have been successfully discussed from this viewpoint.[2,3] In the first of these papers structures were described in terms of shift-lattice distributed fragments of either Au_4Mn or Au_3Mn.[2]

While this approach was entirely successful in its objective of deriving new structural relationships, several aspects were considered by us to need further elaboration. The most important of these related to the nature of the diffraction patterns of the phases. Diffraction patterns of these alloys display shift-lattice like characteristics quite clearly. In our first paper on the topic[2] it was only the Mn atoms that were shown to be shift-lattice distributed. Now because the Mn atoms are in the minority both with respect to composition and in terms of atomic number when compared to the Au atoms it became of interest to see how this could arise. In effect this implied that the arrangement of both atoms in the structure had to be clarified in shift-lattice terms. In the first part of this study[3] a group of one-dimensional structures was investigated and it was shown that both the Mn and Au atoms could be described as lying on shift-lattices with almost identical parameters, thus ensuring that the shift-lattice nature of the structure was clearly displayed in the diffraction patterns.

In this paper the final part of the study is reported. The structures of a number of two-dimensional shift-lattice structures are analysed and it is shown that both the Au and Mn atoms lie on almost identical two-dimensional shift-lattices. Moreover, the relationship between these two-dimensional shift-lattices and the previously described one-dimensional series is revealed for the first time.

Two-dimensional shift-lattice terminology

The shift-lattice approach is essentially a method of constructing and analysing structures in terms of recognisable fragments of a simpler lattice. One dimensional shift-lattices are made up of slabs of lattice of finite width and effectively infinite length arranged in an ordered way. Two-dimensional shift lattices are made up of the stacking of columns of structure, which are usually shown as squares or rectangles in projection.[4] The lattice fragments are contained within a set of *g*-functions which delineate the columns of the lattice. Outside each *g*-function the lattice is not present. The distribution of the *g*-functions is given by two vectors $\boldsymbol{\beta}_1$ and $\boldsymbol{\beta}_2$ and the lattice within each *g*-function is described by the vectors $\boldsymbol{\alpha}_1$ and $\boldsymbol{\alpha}_2$. The lattice within each *g*-function is constrained to have an identical orientation in all cases. A significant feature of the construction is that the lattice contained within each *g*-function is shifted by a characteristic amount on going from one *g*-function to a neighbour.

These features are illustrated in Fig. 1. Each circle represents a lattice point, located on an $\boldsymbol{\alpha}_1\ \boldsymbol{\alpha}_2$ lattice, which need not be orthogonal. The boundaries of the *g*-functions, within which the lattice exists, are shown as rectangular boxes, which can take any shape. These lie on a lattice defined by the vectors $\boldsymbol{\beta}_1\ \boldsymbol{\beta}_2$. On moving parallel to $\boldsymbol{\beta}_1$ the lattice within each *g*-function is shifted by a vector distance $\varepsilon_{11}\boldsymbol{\alpha}_1+\varepsilon_{21}\boldsymbol{\alpha}_2$, which, in the case of Fig. 1 is $0.5\boldsymbol{\alpha}_1+0\boldsymbol{\alpha}_2$. On moving parallel to $\boldsymbol{\beta}_2$ the lattice within each *g*-function is shifted by a vector distance $\varepsilon_{12}\boldsymbol{\alpha}_1+\varepsilon_{22}\boldsymbol{\alpha}_2$ which is $0\boldsymbol{\alpha}_1+0.5\boldsymbol{\alpha}_2$ in Fig. 1. In other directions the shifts are the sums of appropriate multiples of $0.5\boldsymbol{\alpha}_1+0\boldsymbol{\alpha}_2$ and $0\boldsymbol{\alpha}_1+0.5\boldsymbol{\alpha}_2$, as can be judged from the figure (see also, ref. 4).

Some Au–Mn alloy structures

The structure of Au_4Mn, which is of the Ni_4Mo type,[5,6] is shown in Fig. 2(a). The structure of the Au_3Mn composition

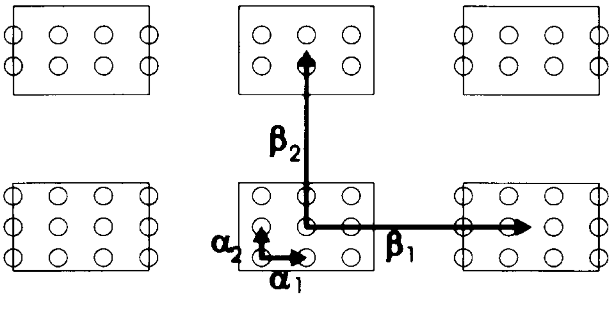

Fig. 1 Schematic illustration of a simple two-dimensional shift-lattice. Each circle represents a lattice point, located on an $\boldsymbol{\alpha}_1\ \boldsymbol{\alpha}_2$ lattice. The boundaries of the *g*-functions, within which the lattice exists, are shown as rectangular boxes. These lie on a lattice defined by the vectors $\boldsymbol{\beta}_1\ \boldsymbol{\beta}_2$. The $\boldsymbol{\alpha}_1\ \boldsymbol{\alpha}_2$ lattice in each box is displaced with respect to its neighbour as explained in the text.

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†Part 1: ref. 3.

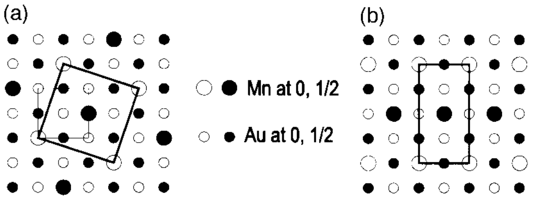

Fig. 2 (a) The Au_4Mn structure (the Ni_4Mo structure). The heavy outline shows the unit cell, and the light outline shows the fcc subcell. (b) The Al_3Ti structure of many fragments of composition Au_3Mn found in Au–Mn alloy structures. The unit cell is outlined. In each diagram the Mn atoms are shown as large circles and the Au atoms as small circles. The filled and open circles occupy heights of 0 and 1/2 in the fcc subcell.

is shown in Fig. 2(b). The structure itself is of the Al_3Ti type.[5,6] There are a number of known Au_3Mn structures, one of which is included in this paper, but no macroscopic phases have yet been synthesised with a composition of Au_3Mn and the Al_3Ti structure. However, in the rather complex two-dimensional structures considered in this paper it is found that fragments of composition Au_3Mn with the Al_3Ti structure are commonplace. For the sake of compactness these two commonly occurring parent structures will simply be referred to as Au_4Mn and Au_3Mn respectively.

The two-dimensional structures which form the subject of this paper are shown in Fig. 3, which focuses upon the Mn atoms only. Fig. 3(a) shows the $Au_{31}Mn_9$-I‡ structure.[7] The squares represent *g*-functions and the Mn atoms within each of these are arranged in exactly the same way as in Au_4Mn. A comparison with Fig. 1 will show that the whole structure is a two-dimensional shift lattice derived from Au_4Mn. The shifts on moving from one g-function to another are quite easy to make out. The structures shown in Fig. 3(b)–(f) are often called lozenge structures. The *g*-functions are diamond shaped and contain fragments of the Au_3Mn structure. The regions between the lozenges are of the Au_4Mn type. It has been shown that all of these lozenge structures can be reproduced by a smooth variation of the two parameters $\boldsymbol{\beta}_1$ and $\boldsymbol{\beta}_2$, although the unit cells, shown as heavy outlines in each diagram, bear no obvious relationship to one another.[2] The final structure shown, in Fig. 3(g), is that of the 'Watanabe structure' of Au_3Mn.[8] It is a two-dimensional shift-lattice with no obvious relationship to the lozenge structures shown. The diagonal *g*-functions, only one of which is drawn, contain fragments of the Au_4Mn structure rather than Au_3Mn.

Note that when drawing these diagrams the atoms have been considered to be points so that those lying near to *g*-function boundaries are correctly assigned. In order to correlate these diagrams with those that follow a reference Mn atom has been stripe-shaded in each figure.

Results and Discussion

$Au_{31}Mn_9$-I

A projection of the structure of $Au_{31}Mn_9$-I[7] is shown in Fig. 4(a). It can be related to Fig. 3(a) by use of the striped 'reference' Mn atom. In addition to the Au_4Mn shift-lattice description which has been illustrated in Fig. 3(a), the structure can be also be divided up into *g*-functions which contain only Mn atoms, as shown in Fig. 4(b). The $\boldsymbol{\alpha}_1$ $\boldsymbol{\alpha}_2$ lattice refers to the underlying fcc structure. Repetition of the *g*-functions using the vectors $\boldsymbol{\beta}_1$ and $\boldsymbol{\beta}_2$ gives rise to a two-dimensional shift-lattice. The actual shifts of the Mn atoms in moving from one *g*-function to a neighbouring one is zero because all Mn atoms occupy sites in the fcc substructure. However, the Mn atoms do not centre each *g*-function because the Mn strips are not evenly spaced throughout the structure.

It is found that the Au atoms can also be fitted into a two-dimensional shift-lattice. The *g*-functions are shown in Fig. 4(c). It is seen that the $\boldsymbol{\alpha}_1$ $\boldsymbol{\alpha}_2$ lattice is the same in all three figures and that the $\boldsymbol{\beta}_1$ $\boldsymbol{\beta}_2$ vectors are identical in Fig. 4(b) and (c). Once again the shifts involved are zero as all Au atoms sit at normal fcc sites. Moreover, the *g*-functions for the Au lattice are complementary to those of the Mn lattice. The long edges of the *g*-functions lie along (120) with respect to the $\boldsymbol{\alpha}_1$ $\boldsymbol{\alpha}_2$ lattice and the only difference is in the widths of the Au-containing and Mn-containing *g*-functions.

It has thus been demonstrated that both sets of atoms lie on very similar two-dimensional shift-lattices and hence that the shift-lattice character of the diffraction pattern will be clear as both atoms contribute almost identical arrays of reflections.

$Au_{31}Mn_9$-L and $Au_{72}Mn_{21}$

The 3 × 3 lozenge structure of $Au_{31}Mn_9$-L[9] is shown in Fig. 3(b). The resemblance to $Au_{31}Mn_9$-I shown in Fig. 3(a) is not pronounced. However, this structure can also be drawn as a set of Mn only containing *g*-functions, as shown in Fig. 5(a). The $\boldsymbol{\alpha}_1$ $\boldsymbol{\alpha}_2$ lattice is again taken as the underlying fcc substructure, and for clarity the Au atoms have not been shown. In this representation the structure looks surprisingly like that of $Au_{31}Mn_9$-L. The long boundaries of the *g*-functions lie along (120), as before. Each *g*-function contains three Mn atoms. The only difference between the structures in this representation lies in the values of $\boldsymbol{\beta}_1$ and $\boldsymbol{\beta}_2$.

It can also be shown that the Au atoms,§ which lie in the spaces between the shaded *g*-functions in Fig. 5(a), are also on a complementary shift-lattice with identical $\boldsymbol{\alpha}_1$ $\boldsymbol{\alpha}_2$ and $\boldsymbol{\beta}_1$ $\boldsymbol{\beta}_2$ parameters. The only difference between the two shift-lattices lies in the widths of the *g*-functions in a direction parallel to $\boldsymbol{\beta}_1$.

The (3 × 3)(3 × 4) lozenge structure of $Au_{71}Mn_{21}$[9] is shown in Fig. 3(c). When this is represented as a set of Mn-only containing *g*-functions, as shown in Fig. 5(b), the close relationship with the last two structures becomes clear. Once again the *g*-functions contain three Mn atoms and the long edges lie parallel to (120) with respect to the $\boldsymbol{\alpha}_1$ $\boldsymbol{\alpha}_2$ lattice. There is a smooth transition between the $\boldsymbol{\beta}_1$ and $\boldsymbol{\beta}_2$ values in all three phases and this is the only significant difference between them. Indeed the difference in the $\boldsymbol{\beta}_1$ and $\boldsymbol{\beta}_2$ values between $Au_{31}Mn_9$-L and $Au_{72}Mn_{21}$, Fig. 5(a) and (b), is so small as to be impossible to see on the figures. It is only when large scale drawings are prepared that the differences become visible. Moreover, as we have described previously, any values of $\boldsymbol{\beta}_1$ and $\boldsymbol{\beta}_2$ between those utilised will give similar but slightly different structures.

It is also true that the Au atoms are also distributed as a two-dimensional shift-lattice. The *g*-functions are complementary to the Mn-only containing g-functions shown in Fig. 5(b).

$Au_{95}Mn_{28}$ and $Au_{27}Mn_8$

The structures of the two lozenge phases $Au_{95}Mn_{28}$ and $Au_{27}Mn_8$[9] are shown in Fig. 3(e) and (f) respectively. They can also be drawn in terms of two-dimensional shift-lattices with complementary Mn-only containing and Au-only containing *g*-functions. The Mn-only containing *g*-functions are shown in Fig. 6(a) and (b).

The similarity between the two diagrams is striking. Moreover, they are also very similar indeed to those shown in Fig. 4(b), 5(a) and (b). The major difference is that the value of $\boldsymbol{\beta}_2$ has increased in $Au_{95}Mn_{28}$ and $Au_{27}Mn_8$ relative to that on the structures discussed above so that four Mn atoms

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‡This nomenclature is chosen to distinguish this structure from that of the lozenge structure of composition $Au_{31}Mn_9$, called $Au_{31}Mn_9$-L.

§For compactness not all the Au-only two-dimensional shift-lattices have been included. The authors will be happy to provide drawings for interested readers.

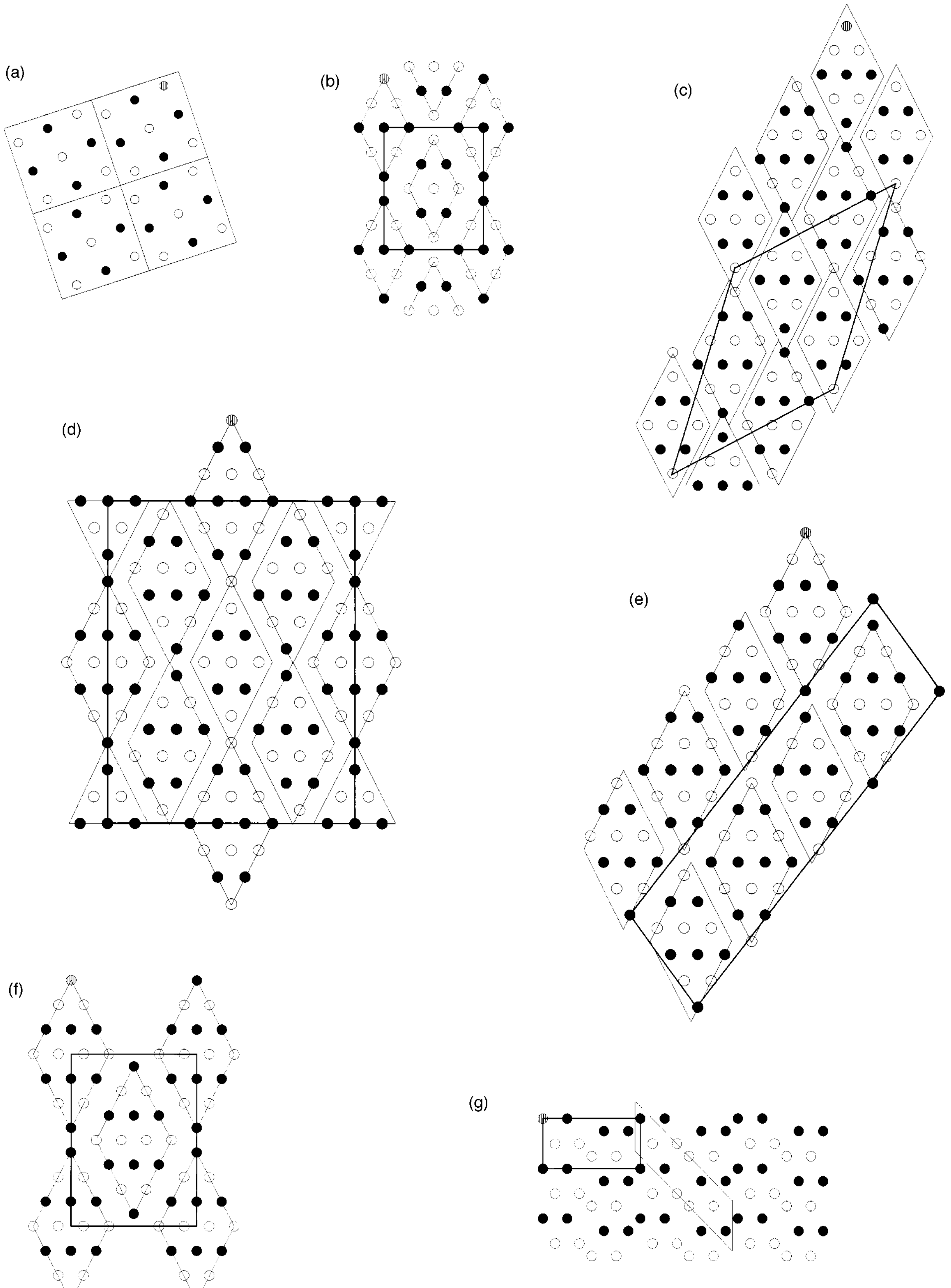

Fig. 3 The Mn atom positions in some Au–Mn alloys which are two-dimensional shift-lattices. The light lines represent the two-dimensional *g*-functions and the heavy lines, when included, show the crystallographic unit cell. Atoms at *z* values of 0 and 1/2 with respect to the fcc subcell are shown as open or filled circles respectively. The striped atoms are for reference with respect to following figures. (a) $Au_{31}Mn_9$-I, (b) $Au_{31}Mn_9$-L, (c) $Au_{72}Mn_{21}$, (d),$Au_{167}Mn_{49}$, (e) $Au_{95}Mn_{28}$, (f) $Au_{27}Mn_8$, (g) Au_3Mn Watanabe.

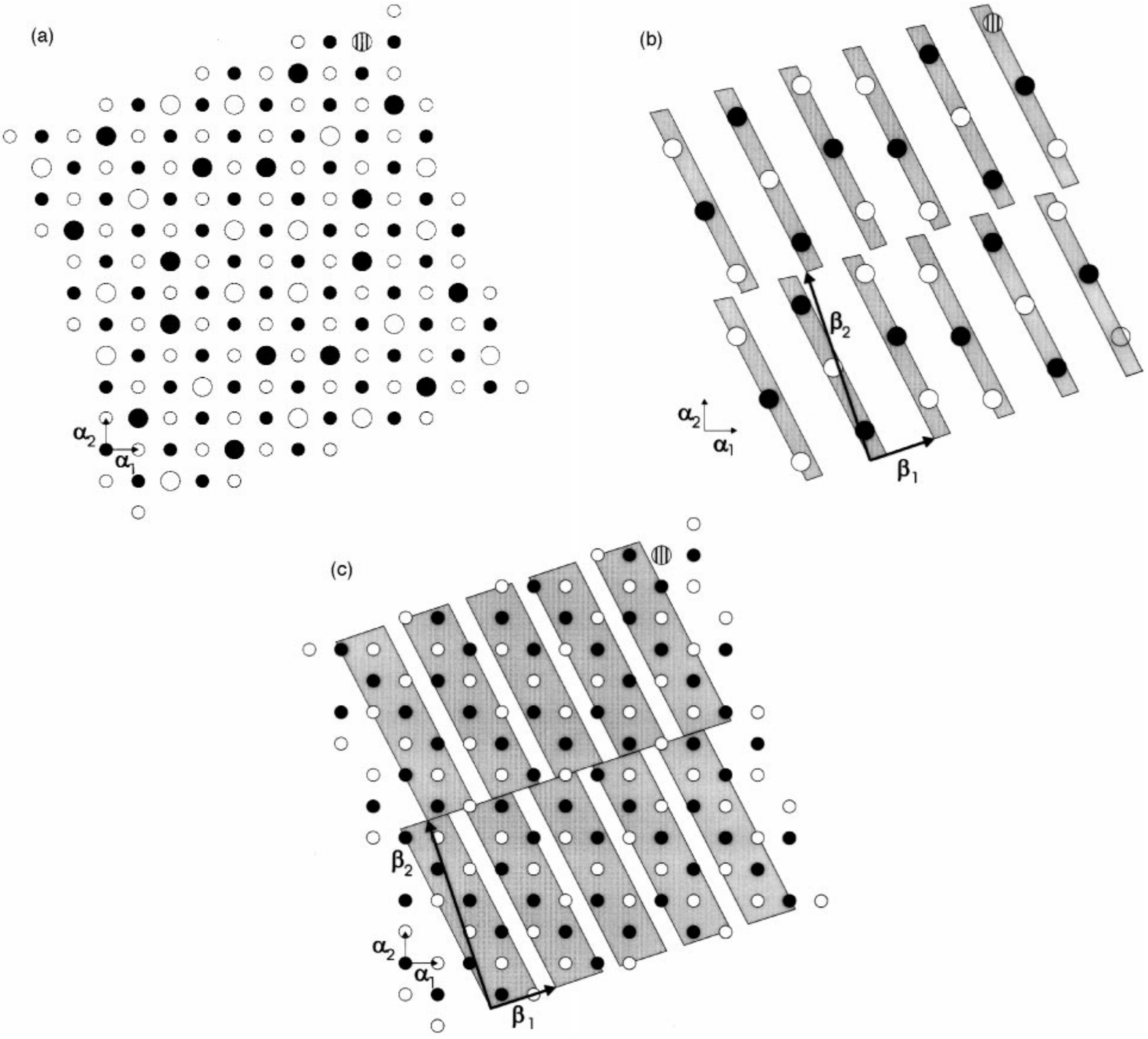

Fig. 4 (a) The structure of $Au_{31}Mn_9$-I, large circles represent Mn and small circles represent Au. Atoms at 0 and 1/2 with respect to the fcc subcell are shown as open or filled circles respectively. (b) The Mn-only containing *g*-functions in the structure shown in (a). (c) The Au-only containing *g*-functions in the structure shown in (a).

occupy each *g*-function instead of three. In other respects the shift-lattice parameters are very similar. In particular the long *g*-function boundaries lie on (120) with respect to the $\boldsymbol{\alpha}_1$ $\boldsymbol{\alpha}_2$ lattice.

$Au_{167}Mn_{49}$

It has been pointed out above that smooth changes in the value of $\boldsymbol{\beta}_1$ while keeping $\boldsymbol{\beta}_2$ (more or less) constant in the $Au_{31}Mn_9$-I, $Au_{31}Mn_9$-L and $Au_{72}Mn_{21}$ group of structures would produce an infinity of structures all of which were two-dimensional shift lattices and all of which would differ infinitesimally from their neighbours in composition. The same situation can occur if $\boldsymbol{\beta}_1$ is kept (more or less) constant and $\boldsymbol{\beta}_2$ is varied smoothly between the value needed to give strips of Mn atoms containing three Mn atoms ($Au_{31}Mn_9$-I, $Au_{31}Mn_9$-L and $Au_{72}Mn_{21}$) as opposed to those containing four ($Au_{95}Mn_{28}$ and $Au_{27}Mn_8$).

Only one example of such a structure has been identified to date, $Au_{167}Mn_{49}$,[9] shown in Fig. 3(d). A drawing of the Mn-only containing *g*-functions, shown in Fig. 7, reveals that the *g*-functions contain three and four Mn atoms alternately in a direction parallel to $\boldsymbol{\beta}_2$. The value of $\boldsymbol{\beta}_2$ lies half way between those appropriate for the three Mn atom strips and the four Mn atom strips. Once again it can be stated that a smooth variation of $\boldsymbol{\beta}_2$ will produce an infinity of phases with a variety of ordered arrangements of strips of three and four Mn atoms repeated in the $\boldsymbol{\beta}_2$ direction.

The relationship between the two-dimensional and one-dimensional structures

In the case of $Au_{167}Mn_{49}$ the value of $\boldsymbol{\beta}_2$ was half way between those appropriate for the *g*-functions containing three Mn and four Mn atoms. If the value of $\boldsymbol{\beta}_2$ is allowed to increase smoothly more and more Mn atoms will be accommodated in the *g*-functions. Eventually these will become infinitely long and so one-dimensional shift-lattices will be formed.[2,3]

All of the diagrams shown in Fig. 4(b) onwards can thus be considered as made up of strips of one-dimensional shift-lattices running parallel to $\boldsymbol{\beta}_1$, a fact confirmed by reference to ref. 3. In particular the strips in $Au_{31}Mn_9$-I are identical to the one-dimensional shift-lattice $Au_{22}Mn_6$.[10] None of the other structures have been observed in synthetic alloys, but is possible to say that the strips in $Au_{31}Mn_9$-L have the one-dimensional shift-lattice structure of an unknown $Au_{10}Mn_3$ ($Au_{3.333}Mn$) and the strips in $Au_{72}Mn_{21}$ are just slightly Mn-richer than this, and the composition of these strips has moved very slightly towards Au_3Mn, to $Au_{23}Mn_7$ ($Au_{3.286}Mn$).

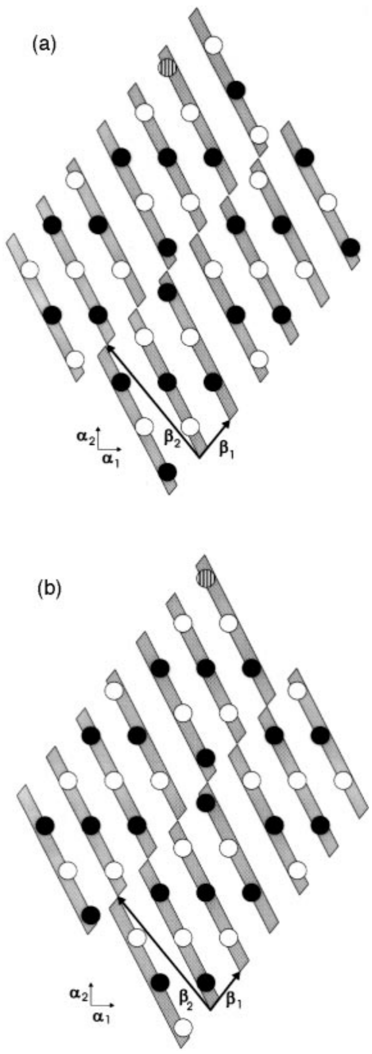

Fig. 5 The Mn only containing *g*-functions in the structures (a), Au$_{31}$Mn$_9$-L and (b) Au$_{72}$Mn$_{21}$

Au$_3$Mn Watanabe

The structure of the form of Au$_3$Mn described originally by Hiraga *et al.*[8] set out as a two-dimensional shift-lattice distribution of Mn atoms in the Au$_4$Mn arrangement is shown in Fig. 3(g). As with all of the other structures considered here it is possible to draw it in terms of Mn-only and Au-only complementary *g*-functions. The Mn containing *g*-functions are shown in Fig. 8. The $\boldsymbol{\alpha}_1$ $\boldsymbol{\alpha}_2$ lattice is the same as before.

The above discussion has shown that an infinity of phases can be described by a smooth variation of either or both $\boldsymbol{\beta}_1$ and $\boldsymbol{\beta}_2$ while maintaining the long-*g*-function boundaries on (120) with respect to the $\boldsymbol{\alpha}_1$ $\boldsymbol{\alpha}_2$ lattice. Naturally an alternative infinity of structures can be produced by a rotation of the *g*-function boundaries from (210) towards (100). The *g*-function boundaries in Fig. 8 lie upon (13,7,0), which is a rotation of only 1.736° anticlockwise from (210). If the *g*-functions were continued indefinitely to create a one-dimensional shift-lattice the structure would lie between those of Al$_3$Ti and Ga$_{13}$Nb$_5$, which is another structure adopted by Au$_3$Mn, the one-dimensional shift-lattice Au$_3$Mn mono-I structure.[2,3] In this case the rotation of the *g*-function boundaries amounts to only 0.754° anticlockwise.

The existence of these two structures with identical composition and very slightly different shift-lattice parameters suggests that the energy difference between them is very small indeed. The vast multiplicity of structures that can be generated by slight alterations in the shift-lattice parameters suggests that many more Au$_3$Mn structures could be generated by suitable cooling or quenching regimes and that any structure so formed might well be extremely sensitive to the preparation conditions employed.

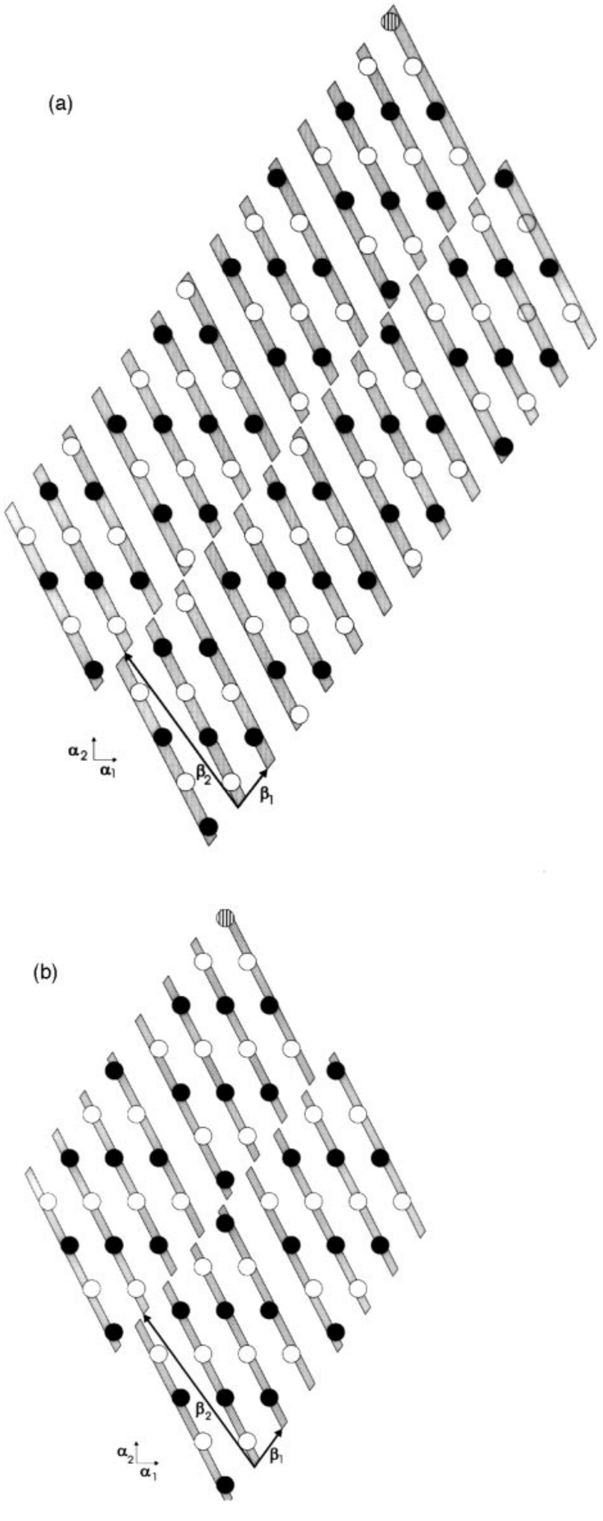

Fig. 6 The Mn only containing *g*-functions in the structures (a) Au$_{95}$Mn$_{28}$ and (b) Au$_{27}$Mn$_8$

Conclusions

The present paper has demonstrated a number of previously unreported facts. (i) All of the two-dimensional shift-lattices in the Au$_4$Mn–Au$_3$Mn composition regions can be considered to be made up of two interpenetrating shift-lattices, one of only Au atoms and one of only Mn atoms. (ii) The parameters of these two shift-lattices are identical except for the width of the

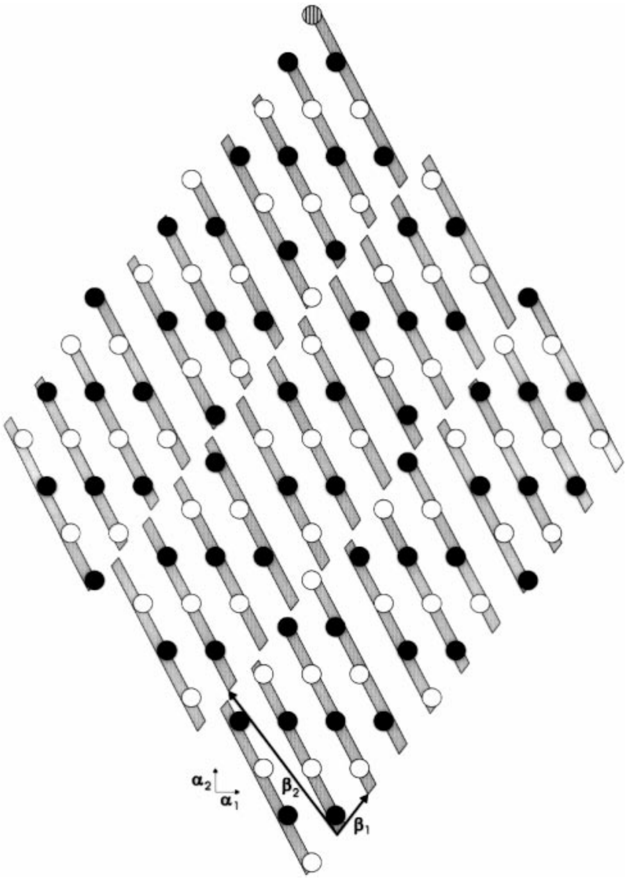

Fig. 7 The Mn only containing *g*-functions in the structure $Au_{167}Mn_{49}$

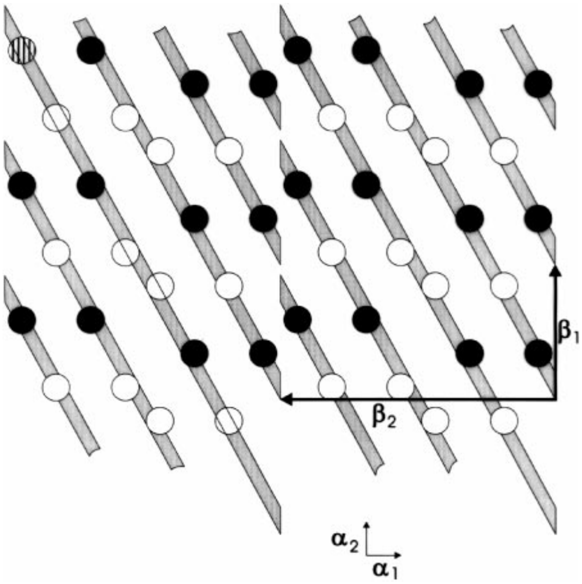

Fig. 8 The Mn only containing *g*-functions in the structure Au_3Mn Watanabe

g-functions of the Au and Mn components. (iii) In view of (ii) the diffraction patterns will display shift-lattice characteristics quite clearly. (iv) The two-dimensional structures described here can all be thought of as made up of strips of one-dimensional shift-lattices. (v) Vast numbers of related structures can be generated by small variations in the shift-lattice parameters.

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