Occurrence of faults/APBs in periodic to quasiperiodic transformations

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Abstract. The strip projection method has been used here to establish the structural relationships between various two dimensional quasiperiodic structures and certain well known periodic structures. These periodic structures, designated as unmodulated approximants, can transform into their quasiperiodic counterparts in a continuous fashion. The early stages of such transformations are characterized by the occurrence of faults or APBs. There is considerable high resolution electron microscopy (HREM) and electron diffraction evidence in favour of this in the case of the β -Mn to octagonal quasicrystal, the σ -phase to dodecagonal quasicrystal and the Al_5Ti_3 to quasiperiodic superlattice structure transformations.

Keywords. Quasicrystals; quasiperiodic superlattices; quasiperiodicity; TiAl intermetallics, antiphase boundaries; faulting; faults; rational approximants; continuous transitions.

1. Introduction

The method of projection from higher dimensional lattices is among the most widely used methods of generating quasiperiodic as well as the related periodic tilings. In this method, the points contained within a suitably defined strip in the higher dimensional lattice are projected onto a lower dimensional hyperplane to generate various tilings of interest. Four different classes of structures result depending upon the orientations of the strip and the projection plane. These are: quasicrystals (both the strip and the projection plane in irrational settings), quasiperiodic superlattice (strip irrational; projection plane rational), periodic approximants of quasicrystals (strip rational and projection plane irrational) and periodic approximants of quasiperiodic superlattices (strip as well as the projection plane rational). The essential difference between a quasicrystal (QC) and a quasiperiodic superlattice (QPSL) is that the latter consists of a quasiperiodic arrangement of tiles of rational dimensions and can therefore be viewed as a quasiperiodic atomic decoration of a disordered underlying lattice (Kulkarni 1989). In the present scheme, rational (or periodic) approximants constitute a continuum of structures which can be generated by a continuous rotation of the strip in the higher dimensional space. The simplest approximant (having the smallest unit cell) is designated as the unmodulated approximant. β -Mn-phase, σ -phase and the Al_5Ti_3 derivative of the off-stoichiometric γ -TiAl phase can thus be viewed as unmodulated approximants of the octagonal and the dodecagonal quasicrystals and the QPSL structure respectively. It is interesting to note that these three unmodulated approximants comprise an identical periodic arrangement of squares and rhombi—the shapes of the rhombi being different in each of these. Occurrence of faults during continuous transitions from the unmodulated to the quasiperiodic phases in these three cases forms the central theme of this paper. Owing to the space limitation, only salient results will be presented here. Details of the projection schemes employed are given in Kulkarni *et al* (1993).

2. Faulting in the β -Mn structure

Most of the pure metals crystallize in the form of relatively simple structures such as fcc (A1), bcc (A2) and hcp (A3). β -manganese and β -uranium (the latter having the well known σ -phase structure), which have relatively complex structures, appear to be noteworthy exceptions to this rule. The atomic arrangement in the β -Mn structure (space group $P4_1 32$) is such that, when viewed in the $[001]$ orientation, the structure can be visualized as a periodic arrangement of two types of tiles— 45° rhombi and squares (Wang and Kuo 1989, 1990). These two types of tiles are present in two different orientations, any given square or rhombus being decorated with an identical arrangement of atoms.

The intimate relationship between the octagonal quasicrystal and the β -Mn structure, both of which are composed of squares and 45° rhombi, deserves a special mention. Twin related variants of β -Mn, which are rotated with respect to each other by 45° , invariably occur in samples of octagonal quasicrystals in Cr–Ni–Si and Mn–Si (Wang and Kuo 1989) alloys. Such twin related domains, when present in a relatively fine state of subdivision, give rise to diffraction patterns of pseudo-eight-fold symmetry which are remarkably similar to those obtained from the octagonal quasicrystal. Another interesting aspect of this relationship is the continuous transformation of the octagonal phase into the β -Mn phase in Cr–Ni–Si (Wang and Kuo 1990).

The strip projection method can be used to establish the structural relationship between the octagonal quasicrystal and the β -Mn phase, and to generate the continuum of structures that are intermediate between the two (Kulkarni *et al* 1993). The orientational relationship between the β -Mn twins and the octagonal quasicrystal, in the structures generated by the projection method, matches precisely with that observed experimentally (Wang and Kuo 1990).

Consider the following unit position vectors in a 4D simple cubic lattice:

$$\begin{aligned} \mathbf{X}_{\text{proj}} &= [1/(2 + 2\theta^2)^{1/2}] [1 \bar{1} \theta \theta]; \mathbf{Y}_{\text{proj}} = [1/(2 + 2\theta^2)^{1/2}] [\theta \theta \bar{1} 1] \\ \mathbf{X}_{\text{virt}} &= [1/(2 + 2\phi^2)^{1/2}] [1 1 \phi \bar{\phi}]; \mathbf{Y}_{\text{virt}} = [1/(2 + 2\phi^2)^{1/2}] [\bar{\phi} \phi 1 1], \end{aligned} \quad (1)$$

where, θ and ϕ are variable indices in the 4D lattice.

These vectors define two 2D subspaces (planes)—the projection plane and the virtual plane, in the 4D lattice. While θ determines the orientation of the projection plane, ϕ dictates the orientation of a strip which is normal to the virtual plane. The octagonal cross section of the strip parallel to the virtual plane (Kulkarni *et al* 1993) is designed to be the convex hull of the projection, onto the virtual plane, of a 4D unit cell centred at the origin of the 4D lattice.

When both θ and ϕ equal the irrational number $\sqrt{2} - 1$ (0.4142136...), the resulting projection is the octagonal quasilattice (figure 1c) which has the forbidden eightfold symmetry. It comprises a quasiperiodic arrangement of squares and 45° rhombi. Two different orientations of the squares and four different orientations of the rhombi can be seen. As the vertices of the octagonal quasilattice are integer linear combinations of basis vectors having irrational orientations in the projection plane (Wang and Kuo 1990), all vertices in the quasilattice have irrational coordinates. The 45° rhombi in the octagonal quasicrystal, which have a minor to major diagonal ratio of $\sqrt{2} - 1$, may be regarded as tiles of irrational dimensions.

Figure 1. Series of 4D to 2D projected structures obtained by continuous rotation of the strip in the 4D lattice. The unmodulated approximants (a) and (e) of the octagonal quasicrystal in (c) constitute 45° twins of the β -Mn structure. Early stages of the continuous β -Mn to octagonal quasicrystal transition are periodically faulted long period modulated structures such as the ones in (b) and (d). Solid squares mark corners of the unit cells of the long period structures in (b) and (d). Faults are outlined with bold lines. Figures are not to scale. Tile dimensions are the same in all the structures.

Different periodic approximants of the octagonal quasicrystal can be obtained by assigning rational values to ϕ . The 0/1 and the 1/1 approximants (figures 1a and e), which constitute two rather simple and also extreme periodic approximants of the octagonal quasicrystal, identify themselves with the 45° twins of the β -Mn structure when the constituent tiles are appropriately decorated with atoms (Wang and Kuo 1989). Each orientational variant of β -Mn contains only one of the two possible sets of perpendicular rhombi and may, for reasons which will become apparent later, be regarded as a unmodulated approximant of the octagonal quasicrystal. An infinite continuum of modulated structures of varying periodicities exist which are intermediate between the β -Mn phase and the octagonal quasicrystal. These may be generated by changing ϕ (the orientation of the strip) in a continuous manner from 0/1 (or 1/1) to $\sqrt{2} - 1$. In general, if ϕ equals p/q ($0 < p/q < \sqrt{2} - 1$), where p and q are relative primes, the resulting approximant has a square unit cell of dimension $2A[(\sqrt{2} - 1)^* p + q]$, where $A = [1/(2 + 2(\sqrt{2} - 1)^2)^{1/2}]$.

The modulated structures, arising during the initial stages of the transformation (corresponding to ϕ values close to 0/1 or 1/1) from the β -Mn to the octagonal phase, are of particular interest as these are long period modulated structures which are closely related to β -Mn. Unit cells of two such structures corresponding to $\phi = 1/8$ and $\phi = 7/8$ are shown in figures 1b and d respectively. These structures contain four modules of a single orientational variant of the β -Mn structure. These four modules are out of phase with respect to one another and are separated by faults comprising linear

arrangements of the 45° rhombi. The faults lie along $[100]_p$ and $[010]_p$, and the fault vectors are of the type $\langle (\sqrt{2}-1)/2, -1/2, 0 \rangle$. The rhombi constituting the fault, it may be noted, have orientations different from those of the rhombi within the modules. Another interesting observation is that the faults themselves become discontinuous (out of phase) at the octagonal 'regions of uncertainty' which appear at the centre of each unit cell. Such regions can be tiled in several different ways. A suitable choice can be made by imparting an infinitesimal shift to the window (Kulkarni *et al* 1993). These regions of uncertainty reduce the overall symmetry of the approximants from $4mm$ to m —the only exceptions being the unmodulated 0/1 and 1/1 approximants which belong to the 2D point symmetry group 4.

3. APBs in continuous periodic to quasiperiodic superlattice transition in γ -TiAl

A periodic to quasiperiodic transformation, which involves structures quite similar to the ones outlined in the earlier section, can also occur in superlattice structures. Here, the orientation of the projection plane is made rational by setting $\theta = 1/2$. The resulting structures, corresponding to ϕ equal to $\sqrt{2}-1$, 0/1 and 1/1, are shown in figures 2c,a and e, respectively. These structures are identical to their counterparts in figure 1 except that one set of perpendicular 45° rhombi in the latter are replaced by fat rhombi in the

Figure 2. (a) Al_5Ti_3 and (e) $Al_{11}Ti_7$ are unmodulated approximants of the quasiperiodic superlattice structure in (c). Approximants (b) and (d) constitute long period antiphase boundary (LPAPB) modulated structures derived from (a) and (e) respectively. The nonconservative APBs are outlined with bold lines. Lean and fat rhombi and squares represent structural units of Ti_2Al , Ti_3Al and Ti_4Al stoichiometries respectively. The series of projected structures from (a) to (e) obtained by continuous rotation of the strip in the higher dimensional lattice represent a continuous superlattice transformation which can be effected by continuously changing the alloy composition from Al_5Ti_3 to $Al_{11}Ti_7$.

former, while the other set of 45° rhombi are replaced by lean rhombi. These rhombi, which have minor to major diagonal ratios of $1/2$ or $1/3$, may be regarded as tiles of rational dimensions. Since the coordinates of the vertices of the tiles in figure 2 are integer linear combinations of the basis vectors having rational orientations in the projection plane (Kulkarni *et al* 1993), they form a subset of the lattice points of an underlying square lattice as depicted in figures 2a and e. If the vertices of the tiles and the remaining points of the square lattice are decorated with two different atomic species, say Al and Ti respectively, it is possible to think of these structures as superlattices of the underlying square lattice. The constituent tiles — the square, the fat and the lean rhombi — may thus be regarded as unimolecular clusters of stoichiometries Ti_4Al , Ti_3Al and Ti_2Al respectively. The QPSL structure in figure 2c, which comprises a quasiperiodic arrangement of Ti_4Al , Ti_3Al and Ti_2Al tiles, has a composition approximately equal to $\text{Ti}_{3.12}\text{Al}$. Unlike in the case of the octagonal quasicrystal, the $0/1$ and the $1/1$ unmodulated approximants of the QPSL represent two different structures of compositions Ti_3Al and $\text{Ti}_{3.5}\text{Al}$ respectively. Whereas the former has Ti_4Al and Ti_2Al tiles in equal numbers (this structure will be referred to as the 4–2 structure), the latter (the 4–3 structure) consists of Ti_4Al and Ti_3Al tiles only.

While the QPSL structure described above has not been observed in any known alloy system to date, its unmodulated $0/1$ and $1/1$ approximants have been found to occur in Al–Ti intermetallics as derivatives of the equilibrium γ -TiAl (L1_0) structure (Loiseau *et al* 1985). A $\{200\}$ plane of fcc comprises a square lattice wherein the sides of the square are defined by $1/2\langle 011 \rangle$ vectors. In the stoichiometric γ phase alternate (002) planes are occupied exclusively by Al or Ti atoms. Replacement of the Ti layers by the 4–2 or by the 4–3 structure gives rise to structures of Al_5Ti_3 or $\text{Al}_{11}\text{Ti}_7$ stoichiometries. Progressive additions of Ti to the Al_5Ti_3 phase have been found to lead to incommensurate superlattice structures which are structurally intermediate between the Al_5Ti_3 and the $\text{Al}_{11}\text{Ti}_7$ phases. The continuous transition from the Al_5Ti_3 to the $\text{Al}_{11}\text{Ti}_7$ phase, which can be brought about by additions of Ti, can be modelled using the strip projection method (Kulkarni *et al* 1993). As in the case of the transition between the β -Mn and the octagonal phases, it involves a continuous rotation of the strip effected by changing ϕ from $0/1$ (corresponding to the 4–2 structure) to $\sqrt{2}-1$ (the QPSL structure), and subsequently, to $1/1$ (the 4–3 structure). Such a rotation of the strip is tantamount to a continuous change in the composition of the projected structures from Ti_3Al to $\text{Ti}_{3.5}\text{Al}$ and represents a continuum of superstructures of varying periodicities (Kulkarni *et al* 1993).

The structures, which correspond to the early stages of the transformation from the unmodulated 4–2 (or 4–3) structure to the QPSL, constitute long period antiphase boundary (LPAPB) modulated structures (figures 2b and d) and are remarkably similar to the faulted structures in figures 1b and d. The structure in figure 2b, which contains marginally higher Ti than the unmodulated and stoichiometric 4–2 structure, comprises four ‘out of step’ modules (translational variants) of the 4–2 structure, separated by Ti_3Al tiles which form antiphase boundaries (APBs) in $\langle 10 \rangle$ orientations. On the other hand, the LPAPB derivative of the 4–3 structure (figure 2d), which contains marginally lower Ti than the unmodulated 4–3 structure, shows $\langle 11 \rangle$ APBs consisting of Ti_2Al tiles. The APBs in figures 2b and d should be regarded as nonconservative APBs, since their introduction in the relevant unmodulated structures leads to a departure from the simple stoichiometries of the unmodulated phases. Such nonconservative APBs represent a possible way of accommodating offstoichiometry in an unmodulated superlattice structure without producing disorder. The period of the

Figure 3. (a) σ -phase—the unmodulated approximant of the dodecagonal quasicrystal in (c), (b) faulted σ -phase structure which represents an intermediate stage of the σ -phase to dodecagonal quasicrystal transition. The faults comprising six-sided holes are in agreement with HREM images of such faults (Ishimasa *et al* 1988).

LPAPB structures and therefore, the spacing between the APBs change as ϕ is varied, which in turn results in a change in the positions of the superlattice reflections. The experimentally observed shifts in the positions of the superlattice reflections (Loiseau *et al* 1985) are consistent with the sequence of structural transformations predicted by the projection scheme discussed here (Kulkarni *et al* 1993).

4. Faulting in the σ -phase

Another periodic structure, based on the tiling pattern of the unmodulated structures discussed in the foregoing, is the σ -phase, which is made up of squares and 60° rhombi (figure 3a). Structures intermediate between this unmodulated approximant and the dodecagonal QC (figure 3c) are faulted structures similar to the one in figure 3b. HREM images of the faulted σ -phase in Ni–Cr small particles (Ishimasa 1988) are in agreement with this structure obtained as a 6D to 2D projection.

5. Conclusions

- (I) Unmodulated approximants of the three 2D quasiperiodic structures—the octagonal QC, the dodecagonal QC and the quasiperiodic superlattice structure—are based on an identical periodic arrangement of tiles.
- (II) Faults/antiphase boundaries are the early stages of the continuous transformations between the unmodulated phases and their quasiperiodic counterparts.

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