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Interfaces in icosahedrally related structures: problems and prospects

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Abstract. Icosahedral quasicrystals are frequently observed to coexist with their related phases like pentagonal/decagonal quasicrystals and rational approximant structures. Owing to this, they have common interfaces. The crystallography of these interfaces needs consideration for providing an aid for their characterization through experiments. The purpose of this communication is to present examples of heterophase and homophase interfaces in quasicrystalline systems and to discuss their structural details in terms of higher dimensional crystallography. Some of the uncommon aspects of these interfaces *vis-a-vis* their crystalline counterparts will be highlighted. We shall conclude by identifying the problems and prospects of further research in this area.

Keywords. Quasicrystals; interfaces; higher dimensional crystallography.

1. Introduction

Interfaces are the least discussed topic in quasicrystalline literature. They appear as two-dimensional defects in three-dimensional solids. The two classes of interfaces observed experimentally pertain to (i) the homophase interfaces or grain boundaries and (ii) the heterophase or interphase interface.

Singh and Ranganathan (1997) have summarized various kinds of interfaces belonging to the above categories in quasicrystalline and their related phases. Donnadieu (1997) and Mandal (1998) have discussed the problem of characterization of interfaces in quasicrystalline and their related systems. The crystallography of interfaces discussed by Bollman (1970) relies mostly on the nature of misfit or matching between the two planar nets across a common boundary. Hence the geometry of crystalline interfaces is predominantly governed by the concepts of the underlying lattice rather than the motif of the structure. Further, the discussion of interfaces in terms of coincidence site lattice will therefore be helpful only so long as the content of the unit cell is small. A class of periodic phases related to quasicrystals known as rational approximant structures (RAS) displays large unit cell and hence the dominant role of the geometry of groups of atoms cannot be ignored. A lack of recognition of this point was the reason for the late realization of typical polycrystalline aggregates (Koskenmaki *et al* 1986) in α-AlMnSi phase with $Pm\bar{3}$ symmetry and having 138 atoms per cubic unit cell of lattice parameter ~ 1·26 nm. Such aggregates having definite orientation relationship have later been analysed by Bendersky *et al* (1989) and Mandal *et al* (1993). They have been given a special name 'hypertwins'. The orientations of various grains in them have been shown to arise owing to the presence of icosahedral motif. This conclusion has been drawn from the fact that the composite diffraction of such a polycrystalline aggregates gives rise to icosahedral symmetry. A closer analysis of the result by Bendersky *et al* (1989) has uniquely proved that the lattice flips but the motif remains parallel across the common interface. This example perhaps supplements the apprehension of Donnadieu (1997) that the crystallography of interfaces in systems having large unit cells must be dealt with differently. The complexity of the situation for quasicrystals is enhanced due to the fact that any quasicrystal grain behaves as a unit cell in the true sense of the term. This means that if we have grown nearly a perfect quasicrystalline grain of ~ 10 nm even then the number of atoms are going to be enormously large in the so called repeat unit. Thus, as stated earlier by the author (1998), lack of periodicity rules out the possibility of utilizing the concepts of registry for characterizing interfaces of any of the aforesaid kind as are applicable for crystalline systems possessing smaller number of atoms in the unit cell.

Having posed the problems, we propose to list the varieties of interfaces possible and observed during the synthesis of quasicrystalline materials. We shall confine ourselves only to those cases which have some relationship with the icosahedral symmetry in real space structures and display strong reflections located at distances having relationship with the golden mean ($\tau = (\sqrt{5}+1)/2$) or its approximant in some direction in reciprocal space. We refer to Ranganathan and Chattopadhyay (1991) for the

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designation of a gamut of structures satisfying the above condition. These are 3d qc (icosahedral phase: IQC), 2d qc (decagonal/pentagonal phases: DQC/PQC), 1d incommensurate structure (e.g. vacancy ordered τ phases in τ_∞ limit) and RAS (e.g. α-AlMnSi and others). These icosahedrally related structures (IRS) form a family in themselves and they are frequently observed to coexist. The simultaneous occurrence of any of the two phases during rapid solidification processing and also under epitaxial growth suggests that the interphase interface in alloys having quasicrystalline forming compositions plays a seminal role in dictating a microstructural characteristic during their processing. Hence there is an urgent need to delineate the issue of its characterization. We shall in particular be taking an example of an epitaxially grown Al–Pd–Mn alloy (Menguy *et al* 1993) having alternate lamellae of IQC and DQC for accomplishment of the above goal. They share a heterophase interface which we designate as I/D interface. There are a number of examples of similar interfaces in IQC and its RAS as well as DQC and its RAS which arise under rapid solidification conditions. Analysis of such interfaces is difficult owing to the various defects which the samples possess as a result of quenched in phason strains. We shall refer to the formation of hypertwins and twin variants of IQC phases as examples of homophase boundary for the sake of completeness. Latter has been reported by Ranganathan *et al* (1989) in Al–Mn system. These have been discussed by Ranganathan *et al* (1993) in detail by adopting a higher dimensional view point.

The purpose of this presentation will be to indicate the limitation of our understanding in dealing with interfaces in qcs and their related systems. It will be argued that the higher dimensional structural description permits a plausible explanation for the crystallography of interfaces in such systems. But the actual characterization demands more involved analysis both in theory and experiments. A comparison between the interfaces formed in crystalline and quasicrystalline systems will be made in relation to the role of motif(s) and lattices/quasilattices. The discussion will close with the suggestion for a paradigm shift in concepts for the 3d description of interfaces.

2. Six-dimensional structural description of IRS

The importance of higher dimensional description of quasiperiodic phases has been brought out by various authors and chapter 3 of Janot (1994) discusses the salient features in relation to the icosahedral quasicrystals (IQC). We have also presented our model for various IRS (e.g. Mandal and Lele 1989; Lele and Mandal 1992) and emphasized the importance of economic and unified 6d approach for IRS (Mandal and Lele 1995).

We present here the essential concepts utilized for unified description of IRS in terms of 6d. Bak and Goldman (1988) noted that complexity arising owing to 3d quasiperiodicity of IQC can be surmounted through a mathematical construct of a 6d cubic crystal compatible with ($m\bar{3}\bar{5}$) symmetry. The structure of IQC in 3d physical space then results on accomplishing a suitable cut through a chosen physical space whose spanning vectors (or basis vectors) are the vertex vectors of an icosahedron. The 6d crystal has motif(s) mostly extended in 3d pseudo space. This is a necessary and novel concept for obtaining structural refinement of IQC in terms of limited number of parameters. It has been shown by us that adopting similar point of view for the entire gamut of IRS requires continuous distortion of the 3d physical spanning vectors as well as the 6d cubic crystal. Owing to this, the icosahedral symmetry breaks and various related structures result. The description of whole range of IRS generated and discussed by us can be accomplished by (i) choosing non-cubic but orthogonal 6d lattices and (ii) suitably orienting the 3d physical subspace within the 6d hyperspace. The six basis vectors chosen parallel to the vertices of an icosahedron are known as spanning vector icosahedron (SVI). We designate the basis vectors by v_i ($i = 1$ to 6). These are parallel to five-fold axes of perfect icosahedron. The 2-fold and 3-fold axes will arise as their combinations. The distortions of SVI in a continuous manner through three distinct routes (cf. Mandal and Lele 1995) give rise to various IRS whose point groups are the subgroups of the icosahedral point groups ($m\bar{3}\bar{5}$). The restoration of desired metrical properties, however, restricts the choice of parameters characterizing the distortion. The experimentally observed structures dictate such a choice. A distortion in physical space does affect the choice of 6d orthogonal cell in a natural way (Mandal 1990). The nature of SVI, 6d orthogonal cell and resulting structures are shown in table 1.

3. Interface characterization of IRS in 6d

In this presentation we adopt the alternate method of interface characterization by an appeal to hypercrystal approach owing to the availability of an unified picture and also economy of description mentioned in the preceding section. The use of the proposed technique in relation to experiment will be discussed first by taking example of IQC/DQC or PQC heterophase interface. This will be followed by a brief description of the homophase interfaces in Al–Mn–Fe–Si RAS and Al–Mn IQC phase.

3.1 *Analysis of interphase interface in Al–Pd–Mn system*

The icosahedral and decagonal phases are formed in same alloy systems with slight change in their composition

Table 1. Nature of distorted SVI and 6d orthogonal cell.

S.N.	Nature of SVI* of 3d physical space	Lattice parameters of 6d orthogonal* cell	Resulting structures
ia	Loss of all the 5-fold axes along 6 vertex vectors	t_1; $t_2=t_5$; $t_3=t_4$; t_6	Phases with (222) symmetry
ib	Restoration of one 5-fold axes symmetry along one of the 6 vertex vectors	$t_1=t_2=t_3=t_4=t_5$; t_6	Pentagonal ($\bar{5}m$) and decagonal (10/m)
ii	Loss of all the 2-fold axes except one	$t_1=t_2=t_6$; $t_3=t_4=t_5$	Trigonal ($\bar{3}m$)
iii	Loss of all the 2-fold axes except one set of 3 mutually orthogonal axes	$t_1=t_5$; $t_2=t_4$; $t_3=t_6$	Orthorhombic (*mmm*)

*For IQC, SVI refers to a perfect icosahedron and 6d cell becomes hypercubic with $t_1=t_2=t_3=t_4=t_5=t_6$.

and experimental conditions. Menguy *et al* (1993) have reported the epitaxial growth of IQC and DQC in an Al–Pd–Mn alloy based on high resolution electron microscopy of their specimen. Similar observations have been reported for other systems based on the composite selected area diffraction patterns recorded from the respective grains of IQC and DQC. We proceed now to correlate their orientation relationship and nature of the interface in terms of unified 6d structural description proposed by us. It is worth mentioning here that the description of 2d quasiperiodic systems require only five basis vectors and hence 5d analysis is sufficient. However, characterization of interfaces like the one being discussed here can never be accomplished by hyperspace description of different dimensions for the two phases in coexistence across a heterophase interface in 3d physical space.

The lattice parameters of 6d hypercubic crystal and that of 6d orthogonal cell are respectively $t_{1I}=t_{2I}=t_{3I}=t_{4I}=t_{5I}=t_{6I}$ and $t_{1D}=t_{2D}=t_{3D}=t_{4D}=t_{5D}$; t_{6D} (see table 1). The subscripts I and D added to indicate that former gives rise to IQC whereas the latter generates DQC. It has been shown by us (Mandal and Lele 1989) that the same orthogonal cell can generate PQC and other related phases by a suitable choice of the motif(s) and its symmetry. However, the discussion of coherency of the two hyperlattices will not be affected by such a detail of structure and we do not elaborate this point further. The hyperspace analogue of two adjoining grains of IQC and DQC will, therefore, mean the coexistence of the two cells with one five-fold axis being common. The 5d interface, thus, created will be a juxtaposition of two hypercubes of varied lattice parameters. Let us suppose that one (t_{6I}) of the 6d hypercubic edges is parallel to the unique five-fold axis (t_{6D}) for the orthogonal cell. As a result of this, any discussion about the registry of the two 5d hypercubic lattices across the interface will similarly give rise to three situations akin to those encountered in 3d crystalline case and these are (i) $t_{1I} \gg t_{1D}$, (ii) $t_{1I} \cong t_{1D}$, (iii) $t_{1I}=t_{1D}$, respectively for incoherent, semicoherent and coherent boundaries.

We now proceed to quantify the consequence of the above during experimental observations. For the sake of continuity we reproduce the basis vectors of SVI from Mandal and Lele (1989)

$$v_6 = |v_6| \hat{Z},$$

$$v_i = |v_1| [\sin \theta T^{i-1} \hat{X} + \cos \theta \hat{Z}], \tag{1}$$

where $i=1$ to 5; T stands for rotation through $2\pi/5$ around Z; $|v_1| = (2/5 \sin^2 \theta)^{1/2}$; $|v_6| = |v_1| [5/2(1-3\cos^2)\theta]^{1/2}$. We know from experiment that $\cos\theta = 1/\sqrt{5}$ for IQC and $\cos\theta = 1/2$ for DQC (Mandal and Lele 1991). Former choice yields $|v_1| = |v_6|$, whereas the latter gives $|v_1| \neq |v_6|$.

The 3d physical direct component (R) of 6d direct lattice vector R^6 can be defined by

$$R^6 = t_1 \sum_{i=1}^{5} m_i\, e_i + t_6\, m_6\, e_6,$$

$$R = t_1 \sum_{i=1}^{5} m_i\, v_i + t_6\, m_6\, e_6, \tag{2}$$

where e_i (for $i=1$ to 6) are orthonormal basis of hypercrystal; sextuplets m_i's are coordinates corresponding to atomic positions. The explicit form of R can be obtained with the help of (1) and (2).

Since the Z-component of R, R_{ZI} of IQC is parallel to R_{ZD} of DQC and their respective grains across the interface share xy quasiperiodic plane in common hence we write the form of xy component for both the cases which obviously do not have any contribution from terms of the type $m_6 t_6$.

The expression for R_{xy} essentially remains same for both the cases and is given by

$$R_{xy} = a_R \left[m_1 x + m_2 \left(\cos \frac{2\pi}{5} \hat{x} + \sin \frac{2\pi}{5} \hat{y} \right) \right.$$

$$+ m_3 \left(\cos \frac{4\pi}{5} \hat{x} + \sin \frac{4\pi}{5} \hat{y} \right) + m_4 \left(\cos \frac{6\pi}{5} \hat{x} + \sin \frac{6\pi}{5} \hat{y} \right)$$

$$\left. + m_5 \left(\cos \frac{8\pi}{5} \hat{x} + \sin \frac{8\pi}{5} \hat{y} \right) \right]. \quad (3)$$

The constant $a_R = t_1 |v_1| \sin \theta$ will be related to the rhombic edge length of the quasiperiodic tiles in the xy plane and can be experimentally determined. Let us say a_{RI} and a_{RD}, respectively denote the edge lengths of the rhombic tiles for the two cases then

$$\frac{a_{RI}}{a_{RD}} = \frac{t_{1I} |v_1|_I \sin \theta_I}{t_{1D} |v_1|_D \sin \theta_D}. \quad (4)$$

Since $|v_1|_I \sin \theta_I = |v_1|_D \sin \theta_D$, thus the ratio of the edge length of the tiles will directly relate the 6D hypercubic parameter t_{1I} and one of the orthogonal cell parameters t_{1D}. In other words, we may calculate a_{RI} and a_{RD} values directly and indicate the nature of the coherency in 6d hyperspace. The interface observed by Menguy *et al* (1993) in Al–Pd–Mn system should be treated as semi-coherent from the theoretical angle since $t_{1I} \neq t_{1D}$. However, experimentally such an interface will be totally coherent and it will be difficult to see the signature of misfit dislocations at the boundary. This can be understood by recalling that the physically observed interface arises owing to the layers having 5-fold symmetry only. It inherits this from the registry of the 5d hypercubes as mentioned earlier. Accordingly, the physical space interface plane is parallel to (111110). The nature of planar quasiperiodic building block for PQC/DQC and IQC cannot be qualitatively different in the layer containing five-fold symmetry owing to relatively similar density and compositions for these phases. The misfit dislocation at the interface will be introduced at every mth step given by $m = n |a_{RI} - a_{RD}|^{-1}$, where n is an integer. The misfit dislocation will be parallel to the edges of the rhombii and their 6d hyperspace direction will be of the type $\langle 1\bar{1}0000 \rangle$. The observation of misfit dislocation will however be dependent on the magnitude of $|a_{RI} - a_{RD}|$.

Above analysis is applicable for a special type IQC/DQC interface for epitaxially grown materials. The nature of interface is going to be entirely different whenever the growth direction of the two phases is different. Such a condition is more prevalent under rapid solidification processing of the alloys. The analysis will then differ in a qualitative way as the interface plane will result owing to registry of a quasiperiodic layer of IQC with the (quasiperiodic + periodic) layer of DQC. The details of characterization can be accomplished by (i) determining the orientation relationships of the two phases by taking composite electron diffraction patterns and (ii) comparing the edge lengths of the appropriate tiles based on the expression of relevant physical direct space components. We shall revert to this in § 4.

3.2 *Hypertwins in Al–Mn–Fe–Si rational approximant structures*

The observation of regular polycrystalline aggregates in Al–Mn–Fe–Si alloys by Bendersky *et al* (1989) demanded a fresh look at the formation of homophase interfaces. They came out with an explanation unheard of in the paradigm of Bollman (1970) by clearly identifying the role of the content of unit cell in giving rise to only five variants of such a phase. The rotation of the lattice by 72° along a direction parallel to the five-fold axis of the icosahedral motif leaves it unaltered and continuous across the grain boundary but changes the orientation of the lattice. This has also been understood on the basis of higher dimensional approach. We refer the reader to Ranganathan *et al* (1993) for further details.

3.3 *Icosahedral twins*

The observation of two twin related grains of IQC in Al–Mn (Ranganathan *et al* 1989) corresponds to a nearly plane homophase boundary. However, this differs from the previous one as both the variants have a quasiperiodic arrangement of atoms. This has been analysed based on the description akin to that of a dichromatic pattern in bicrystallography. Their coexistence must be attributed to the complex interplay of quasilattice and its decoration.

4. Discussion on interfaces in IRS

The two-dimensional boundaries discussed in the above § in quasicrystalline and their related systems pose problems in their analysis owing to the lack of periodicity for the qcs and large unit cell of their related RAS. Let us discuss the nature of interfaces in a system where at least one of the participating phases possesses quasiperiodicity. This rules out the possibility of utilizing the concept of registry of lattices across it for interface characterization. We have kept such a concept intact by recovering the so called hidden hyperlattices (periodic lattices in 6d to be more precise) and geometrical analysis is achieved. Thus we conclude that Bollman (1970) paradigm for interface characterization remains valid in 6d approach. This is true due to the fact that only two motifs per lattice point are needed to obtain atomic positions for the RAS and IQC in 6d hypercube (Cahn *et al* 1988). Also the main and puckered layers as predicted by Steurer (1989) based on Patterson synthesis for the Al–Mn DQC are reproduced by two motifs per lattice point in the 6d orthogonal cell (Mandal and Lele 1991). Although these sound terse but are relevant from the point of view of consistency of geometrical crystallography. We close this discussion by noting that one or two motifs per lattice point irrespective of dimension permits the predominant role of lattice in characterization of interfaces. However, this does not seem to solve the problem of energetics which is solely governed by the bond breaking across the interface. In any case only those possibilities will be frequently observed which cost low energy. This would definitely require the nature of quasilattices and their decoration in physical space. The *I/D* interface discussed by us in this presentation demonstrate that the similarity of planar nets and their decorations perhaps dictates its habit and thereby their substructures. Such a discussion rules out the possibility of observing a condition of unrelated growth of the grains of IQC and DQC under normal solidification condition. If this is proved experimentally for various systems then nearly identical quasiperiodic net and their decoration in that plane for IQC and DQC will eventually be established.

We shall now discuss the example of homophase interface in RAS. The hypertwins offer a clear cut evidence of predominant role of motif in large unit cell structures. The orientation relationships between the two variants in Al–Mn–Fe–Si system have been shown to be dictated by the unit cell content. Do we have similar situation in quasilattice and its decoration? The geometry of the former is dictated by (i) choice of two or more units and (ii) matching rules to ensure quasiperiodicity and global noncrystallographic symmetry whereas the latter is governed by (a) radii of various atoms (b) valency and (c) nature of bonding. Can we really observe the effect of two factors experimentally as encountered for hypertwins? Let us deliberate on this problem further. The periodic lattice gives rise to discrete location of points in reciprocal space in contrast to the quasilattice which would leave the reciprocal space uniformly and densely filled. It is important to note that the two conclusions are independent of the magnitude of lattice and quasilattice parameter(s). The effect of decoration by atoms in conformity with the requisite symmetry of the structures does not change the geometry of the reciprocal lattice of the former but qualitatively affects the latter by making it discrete during diffraction analysis. Hence we see the discrete point group invariance for both the cases. Thus for any quasiperiodic order in solid, there does not seem to be a point in discussing the quasi-lattice and its content separately. Hence the analogue of hypertwins in quasicrystalline materials is not a possibility.

Ranganathan *et al* (1993), Mandal *et al* (1993) and Mandal (1998) have emphasized the characterization of various interfaces observed in IRS on the basis of hyperspace approach which gives answer related to geometrical crystallography but does not promise any answer posed earlier regarding the selection of a particular interface during processing. The 3d structural characterization through simulation by increasing the size of the relevant RAS corresponding to the phases sharing a common interface is the only answer to such questions. However, such an analysis will suffer the criticism of a true long range quasiperiodic order. These are the problems of interface characterization in IRS and demand coordinated efforts of the two descriptions viz. (i) the quasilattice and decoration and (ii) hyperspace structural modelling. The test ground of convergence is experiment. For this, more studies akin to those of Menguy *et al* (1993) on better samples for different alloy systems need to be carried out. Such an effort will be helpful in unravelling the underlying mechanism of microstructural evolution in IRS and also their properties.

5. Conclusions

We have discussed the importance of hypercrystal approach for understanding the geometrical aspects of characterization of heterophase and homophase interfaces in IRS. We have also presented the problems in such a description in delineating the issue of role of interfaces in the microstructural evolution during the processing of such samples. We have finally come to the conclusion that 3d and hypercrystal structural description should supplement each other for unravelling the underlying mechanism of the growth of a particular interface. We have emphasized the importance of HREM studies of defect free samples for a wide range of alloy systems to attain useful understanding in the challenging and fascinating area of interface characterization in IRS.

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