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Ordering transformation in icosahedral quasicrystals and related crystalline phases

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Abstract. Arcs of diffuse intensity appear in various shapes and positions in the diffraction patterns from the icosahedral phase, violating the parity rule for simple icosahedral (SI) symmetry. In the process of annealing treatment, the diffuse spots also evolve in the centre of the arcs and become sharp. These extra diffuse spots change the symmetry of the quasilattice from *P*-type to *F*-type. The ordered and disordered structures in quasicrystal have been linked to the ordered and disordered structures present in the crystalline α (Al–Mn–Si) and α (Al–Fe–Si) alloys.

Keywords. Quasicrystals; rational approximants; ordering.

1. Introduction

While studying the metastable phase formation in rapidly solidified aluminium-transition metal alloys, Shechtman *et al* (1984) discovered the icosahedral phase which is also known as an icosahedral quasicrystal (QC) (Levine and Steinhardt 1984). This phase shows 5-fold, 3-fold and 2-fold rotational symmetries corresponding to the icosahedral point group ($m\bar{5}3$) in reciprocal space. The corresponding Bravais lattices compatible with this point group have been identified in 6-dimensional (6D) space. Rokhsar *et al* (1987) have shown that there are three possible cubic space lattices in 6D space similar to those in 3D space. These are (i) simple cubic (SC), (ii) body centred cubic (BCC) and (iii) face centred cubic (FCC). The 6D cubic lattices i.e. SC, FCC, BCC after projection on irrational orientation onto 3D space can give rise to simple icosahedral (SI), face centred icosahedral (FCI) and body centred icosahedral (BCI) structures respectively.

Most quasicrystals belong to the SI model. However, quasicrystals in Al–Fe–Cu (Ishimasa *et al* 1988), Al–Cu–Cr, Al–Cu–Mn, Al–Cu–Fe (Ebalard and Spaepen 1989, 1990) and Al–Pd–Mn (Tsai *et al* 1990) alloys conform to the FCI model in real space and BCI model in reciprocal space. FCI ordering has been reported for Mg-base alloys by Nikura *et al* (1993). Ishimasa (1995) recently reported that the FCI quasicrystal in Al–Mn–Pd alloy orders further at low temperatures to give rise to a SI quasicrystal. This is also described by him using a six dimensional diamond lattice. The lattice parameters of FCI, SI and diamond lattices are related to each other.

Many other subtle features in the diffraction patterns of the icosahedral phase have been recorded in the literature. The issues raised by these anomalies are critical, as they can resolve the controversy surrounding the concept of quasicrystals (Mukhopadhyay 1990). Mukhopadhyay *et al* (1987) observed the occurrence of diffuse intensity in electron diffraction in Mg–Al–Zn and Al–Mn alloys. Denoyer *et al* (1987) showed that

diffuse intensity exists in X-ray diffraction patterns from Al–Li–Cu alloys. The appearance of the diffuse intensity was reported by Mandal *et al* (1991) in Fe–Ti (also to be seen in the diffraction pattern of Dong *et al* 1986), Kelton *et al* (1988) and Bhaskaran *et al* (1993, 1994) in Ti–Mn and Swamy *et al* (1989) in Al–Cr and also Mukhopadhyay *et al* (1992) in Al–Fe–W. By systematic heat treatment Mukhopadhyay *et al* (1989) have shown that the arcs in Al–Mn alloys lead to an ordering transformation. This was also observed by Ebalard and Spaepen (1990) and Koster and Liu (1993). Hiraga *et al* (1989) found the order–disorder transition temperature in Al–Cu–Ru system. It is of interest to mention that Tsai *et al* (1990) noticed the ordering transition by replacing Al by Pd in Al–Pd–Mn alloys. The aim of the present investigation is to probe the evolution of ordering in quasicrystals and to establish a link with the ordering in related crystalline prototype structures of α (Al–Mn–Si) and α (Al–Fe–Si).

2. Diffuse intensity and superlattice spots in diffraction patterns

The 2-fold diffraction pattern (figure 1a) from as quenched quasicrystalline phase in Al–10% Mn reflects the disordered SI symmetry. However, on aging diffuse intensity appears in the diffraction patterns (figure 1b) which shows arcs of diffuse intensity in the 2-fold patterns from Al–10% Mn, aged at 325°C for 45 min. Figure 1c shows 2-fold pattern exhibiting the extra diffuse spots or weak intensity spots along 3-fold and 5-fold directions. On the other hand, 5-fold and 3-fold zone axis patterns do not show any observable change and the diffuse intensities are absent in these patterns. A detailed analysis of the location of the arcs of diffuse intensities indicates that they occur only along odd parity directions. If we consider the centres of these intensity distribution, a 'τ' inflation scheme describes both the fundamental spots and the centres of these diffuse arcs (figure 1b). Further analysis indicates the presence of diffuse spots in the centres of the arcs (marked by arrow). The co-existence of the diffuse arcs and diffuse spots is noticed for the first time after careful analysis of the diffraction patterns. In figure 1c the diffuse arcs disappear, while the diffuse spots in the centre become intense and sharp enough to be identified. These extra spots violate the parity rule for the SI symmetry in the diffraction pattern. The extra spots along 5-fold direction can be indexed based on BCI symmetry and this confirms the parity rule for FCI in real space. The diffraction pattern from the ordered quasicrystal (Al–Fe–Cu) has been displayed in figure 1d to compare with figure 1c. From the analysis of these diffraction patterns, it appears that the degree of long range FCI ordering is zero in figure 1a and one in figure 1d, and it is intermediate in figures 1b and c. In other words, figures 1b and c can be considered as partially ordered states while the degree of ordering is more in figure 1c as there are no diffuse arcs present. However, in Al–10% Mn system, to attain fully ordered state or perfect long range ordering is inherently difficult. The intensity of the superlattice spots is not as bright as those in Al–Fe–Cu. Experimental results indicate that the replacement of Al by transition metal (other than Mn; for example Pd) plays an important role in the ordering process. In Al–10% Mn as the transition element is less, the perfect long range ordering may not be possible.

Figures 2a and b show two-fold diffractions from disordered and ordered α (Al–Mn–Si) crystals. The former is isostructural to α (Al–Fe–Si) phase, being BCC. By comparing both the diffraction patterns, one can find out the extra spots in figure 2b. Though the point group symmetry is the same for both the cases, the Bravais lattices are

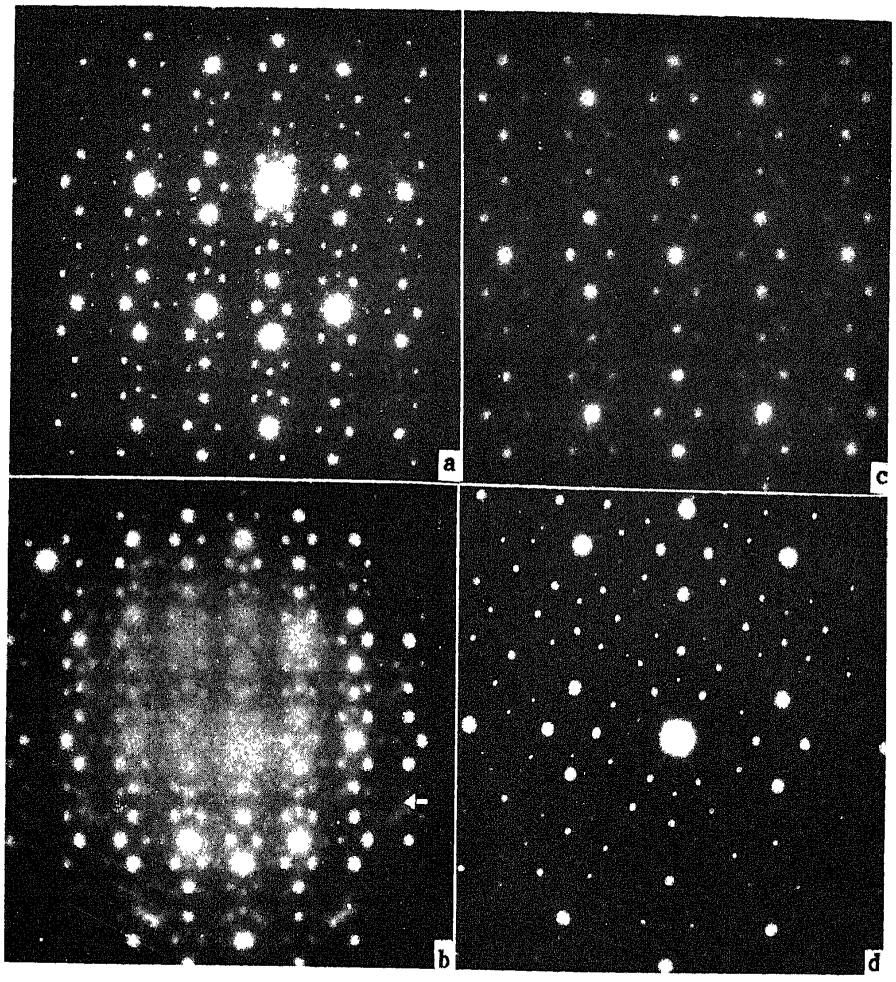

Figure 1. Two fold diffraction patterns from (**a**) disordered Al–10% Mn quasicrystals, (**b**) partially ordered showing the diffuse arcs and also diffuse spots obtained from Al–10% Mn QC, aged at 325°C for 45 min, (**c**) partially ordered Al–10% Mn alloy, aged at 325°C for 45 min (but from a different region of the sample), showing the diffuse spots and (**d**) fully ordered QC from Al–Fe–Cu system.

different. The diffraction pattern from ordered α (Al–Mn–Si) confirms SC symmetry whereas the other one has BCC symmetry. However, both are related by the ordering reaction similar to CsCl-type structure. This can be compared with the computed patterns obtained from 1/1 projection of 6D SC and 6D FCC structures. The similarity between figures 2a and b and 3a and b can be noted. This will be discussed further in the later section.

3. Face centred ordering ($P \rightarrow F$)

At present from the systematic experimental data it can be understood that the arcs of diffuse intensity and the subsequent appearance of spots with τ inflation are related in

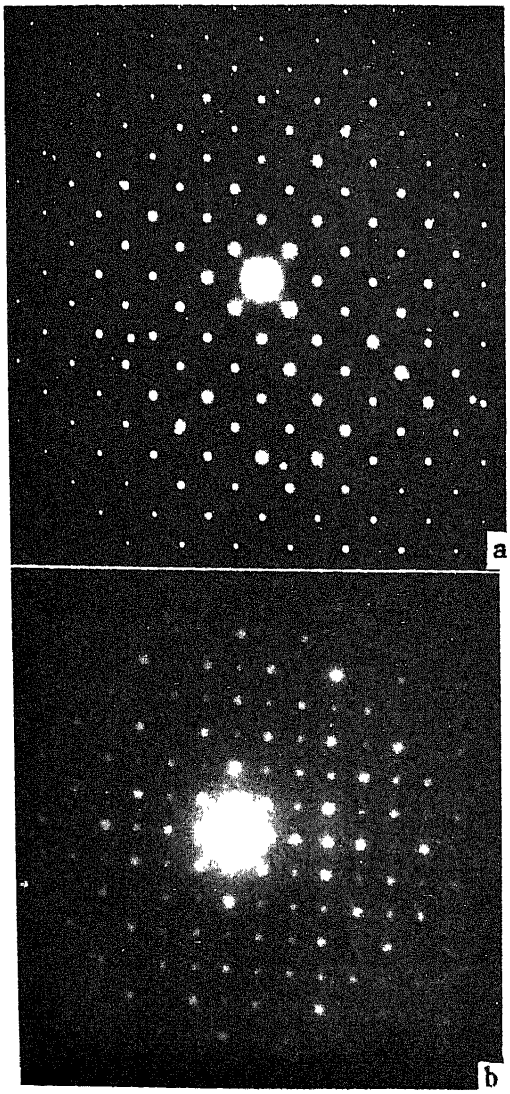

Figure 2. The 2-fold crystalline patterns from (**a**) disordered BCC approximant: Al–Mn–Si and (**b**) ordered SC approximant: α (AlMnSi) structures.

the transition metal systems for which Al–Mn–Si is a prototype. A possible model has been put forward by Cahn (1987) and Henley (1988) independently. According to this model the superlattice ordering will take place in SI quasilattice and it will lead to FCI in real space. Therefore, the disorder–order reaction can be realized in reciprocal space through diffuse spots in the centre of the diffuse arcs:

$$\text{SI}\,(a_{\text{R}}) \rightarrow \text{diffuse spots} \rightarrow \text{BCI}\,(2a_{\text{R}}).$$

The present ordered structure in 6D can be imagined as NaCl type structure. On disordering, the cell parameter is reduced to half the original size. The odd parity spots represent the superlattice positions and the even parity describes the fundamental positions. The quasilattice constant of the ordered QC is twice the previous one.

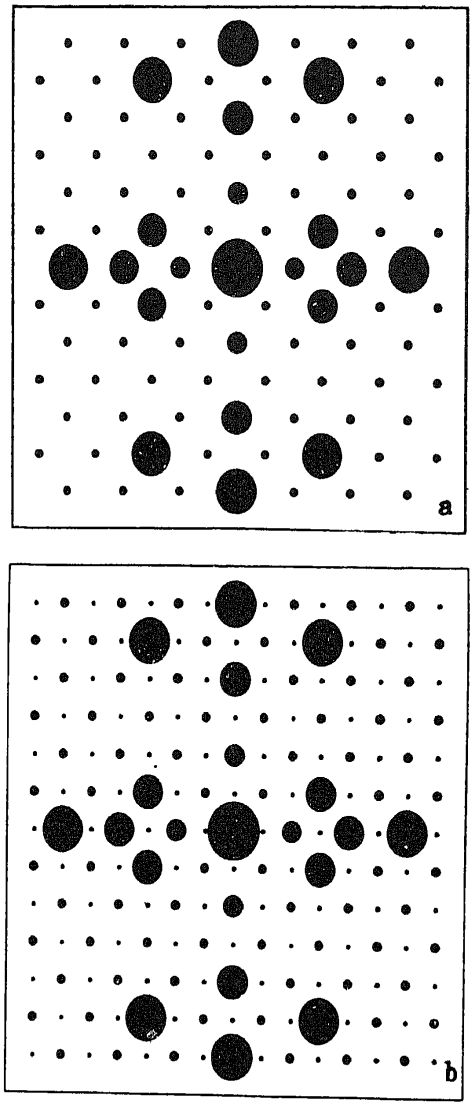

Figure 3. Computed diffraction patterns for (**a**) disordered 1/1 structure and (**b**) ordered 1/1 structures. These have been generated from 6D reciprocal spaces. The intensity reflects the intrinsic structure factor. Geometrical structure factor has not been considered.

It is of interest to note that in some of the Ti- and Mg-based quasicrystals where the diffuse arcs are similar to those of Al–Mn system, the superlattice spots could not be observed. It has been shown by Kelton and Gibbons (1992) that diffuse arcs do not vanish and are present even in the rational approximant structure of the Ti-base quasicrystals. This rational approximant has the same crystal structure as α-AlMnSi. A disordered rational approximant has not been reported in Ti-base alloys.

In the work on Al–Li–Mg alloys by Nikura *et al* (1993) an ordered phase was observed, though no arcs or diffuse intensity was reported. As the rational approximant for this alloy would be a Frank–Kasper phase, the explanation that the ordering of the

quasicrystal is related to the ordering in the rational approximant will not apply to this alloy. Further studies of this alloy are warranted.

4. Link between the ordered and disordered crystals and quasicrystals

We propose that the face centred ordering which has been discussed in earlier section is intimately linked to the ordered and disordered structure in crystalline α (AlMnSi) and α (AlFeSi) alloys. The α (AlMnSi) is described by a SC structure with space group $Pm\bar{3}$ and α (Al–Fe–Si) is BCC with space group $Im\bar{3}$ (Cooper and Robinson 1966; Cooper 1967). In fact, α (AlMnSi) can be treated as an ordered form of α (AlFeSi). While Mn and Al sites in the former are related, some sites in the latter case are unpaired making the structure disordered (Mandal 1990). The order–disorder reaction linking these two structures has been observed by Legresy *et al* (1986) in Al–Fe–Si alloy by electron beam heating.

It is well known that rational approximant structure can be generated by projection from hyper dimensional structure onto rational orientation. Thus, α (Al–Mn–Si) is a 1/1 SC approximant and α (Al–Fe–Si) is 1/1 BCC approximant. 1/1 SC approximant is generated from ordered FCI quasicrystal and 1/1 BCC approximant can be generated from disordered SI quasicrystals. Figure 3(a,b) shows the [100] zone axis corresponding to BCC and SC structures. The extra superlattice spots can be visualized from the diffraction patterns. They also correspond to the patterns from α (Al–Fe–Si) and α (Al–Mn–Si) respectively. It is thus possible to infer that the disordered and ordered structure seen in 3D has its analog in 6D as per the scheme shown in figure 4. This illustrates the link between the order–disorder transformation in quasicrystals and crystals. It is thus possible to observe the ordering reaction by suitable annealing or alloying treatment. A recent paper by Donnadieu *et al* (1994) lends further authority to the above suggestion. They studied a set of Al–Mn–Fe–Si alloys, where the Mn/Fe ratio was varied. In the crystals for low values of Mn/Fe selected area diffraction patterns showed a noticeable diffuse scattering due to short range ordering. As the Mn/Fe ratio is increased the diffuse rings are replaced by weak superlattice spots.

It is pertinent to point out that our identification of the 1/1 rational approximant for the FCI quasicrystal is at variance with that of Khare *et al* (1995). In an investigation on Al–Cu–Cr alloys they found crystalline bcc ($a = 12{\cdot}6$ Å, disordered), simple cubic ($a = 12{\cdot}60$ Å, ordered) and another bcc ($a = 25{\cdot}20$ Å) phases. They identified the first two phases as 1/1 rational approximants of SI quasicrystal and the second bcc phase

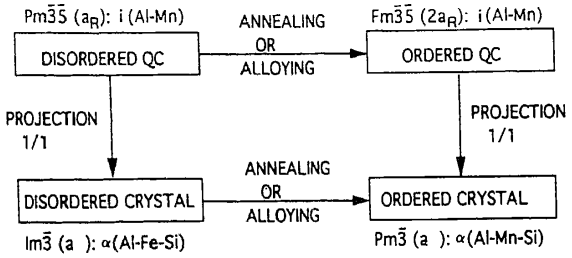

Figure 4. Schematic diagram showing the link between disordered and ordered forms of quasicrystals and crystals.

with twice the lattice parameter as the 1/1 rational approximant of the FCI quasicrystal. It is perhaps likely that this rational approximant structure corresponds to the second ordering reaction observed by Ishimasa (1995). Further study is required to confirm this speculation.

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