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# Quasicrystal–crystal interfaces in bulk materials

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## Abstract

The formation of interfaces of simple crystals with icosahedral quasicrystals has been described. Crystals take on various orientation relationships (ORs) with the quasicrystals in order to make low energy interfaces by matching close packed planes across the interfaces. In the icosahedral phase the closest packed planes are fivefold and twofold. Among various possibilities, an OR will get selected by the surface on which nucleation of a phase occurs. Since one of the phases is quasicrystalline and the other is crystalline, even within the same OR there are variations of several degrees. The high symmetry of the icosahedral phase ensures many possible orientations for planar matching with another phase. The quasiperiodicity ensures an epitaxy with periodic planes of many possible spacings at the interface. Epitaxy can be observed as coincidence of spots in the reciprocal space and verified by imaging in high resolution electron microscopy. In this article examples of interfaces of Al–Cu–Fe icosahedral phases with lead, bismuth and tin, and Mg–Zn–Y icosahedral phases with magnesium are shown. The high symmetry of the icosahedral phase ensures that epitaxy is produced on nearly all interfaces in bulk. Slight misorientations across interfaces are accommodated by dislocations.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

After the stable icosahedral phase was discovered [1], it became apparent that the quasicrystalline phases can occur in equilibrium with crystalline phases. This meant that the quasicrystalline phases could also form a definite interface when coexisting with a crystalline phase in equilibrium. In aluminum alloys the quasicrystalline phases are surrounded by intermetallic phases in the phase diagram, which are often nearly as complex as the quasicrystalline phase. These complex intermetallic phases can be described as approximants to the quasicrystal [2–5]. This approximation fixes the orientation relationship with the quasicrystal. Approximant phases for the icosahedral quasicrystals are cubic or orthorhombic, and their coordinate axes are parallel to three mutually perpendicular twofold axes of the icosahedral quasicrystal. Approximant phases are composed of similar atomic clusters with icosahedral shapes, and therefore a good match at the interfaces is expected. In this article

we will concentrate on interfaces of icosahedral quasicrystals (i-phase) with simple crystals such as elemental metals, which show various orientations with the i-phase and a variety of interfaces. Interfaces in the bulk materials can be studied by a variety of techniques involving transmission electron microscopy (TEM), such as diffraction along various directions with tilting goniometers and high resolution imaging.

An icosahedral phase can exist in metastable equilibrium with aluminum matrix in alloys formed by rapid solidification. In such cases, several orientation relationships between the icosahedral phase and the cubic matrix are possible [6–10]. In the case of magnesium alloys, the icosahedral phase can occur in direct equilibrium with the hexagonal magnesium matrix [11]. Elemental lead [12–14], bismuth [15] and tin [16, 17] can occur in the Al–Cu–Fe matrix due to immiscibility with all (or some) of the matrix elements. They form examples of interfaces of cubic, rhombohedral and tetragonal crystals, respectively, with an icosahedral phase. The energies of these interfaces are reflected in

melting and solidification studies by differential scanning calorimetry (DSC) [13–17]. Strong interfaces between *i*-phase and crystalline matrix can also be used to make strong materials [18–20].

Interfaces with thin films as substrates have been dealt with in another article in this volume [21], as well as the interpretation of the structure of these interfaces [22]. Energies of such interfaces in perfect orientations have been shown by calculations [23]. Such perfect orientations as in thin films do not occur at all surfaces in bulk materials.

The six-integer indexing system of Elser [24, 25] has been followed here to refer to planes and axes. Since the Al–Cu–Fe and Zn–Mg–RE icosahedral phase are ordered, the indices are double those shown by Elser [26]. In addition to the major planes/axes of fivefold, threefold and twofold symmetry, another zone axis will often be referred to here [27], in which a fivefold reciprocal vector intersects a twofold vector at right angles. These zone axes  $\langle \tau 10 \rangle$  in Cartesian coordinates occur at  $90^\circ$  to fivefold axes  $\langle 1\tau 0 \rangle$  (not equivalent indices in three dimensions).

## 2. Orientation relationships between crystals or with a quasicrystal

When a phase with a certain crystal structure is embedded in another crystal (such as precipitates in a matrix phase), then the two phases show a crystallographic relationship by assuming a certain orientation with respect to each other, which determines the interface formation between the two. Orientation relationships (ORs) occur between two crystals so as to minimize interfacial energies. Low energy interfaces are formed between close packed planes of the two crystals. Close packed directions in these two planes are also matched at the interface [28]. When more than one OR is possible, the OR may be decided by the nucleation event on a particular plane [29]. Close packed planes in a crystal can usually be recognized as those with highest intensities in powder diffraction patterns. They are low energy planes. Crystals are usually faceted on these planes, and interfaces form on them. Thus ORs occur between two crystals so as to match these close packed planes. The ORs also determine the morphology of the phases in such a way as to maximize the area of the low energy interfaces. The morphology of the phases, in turn, influences the properties of the bulk materials.

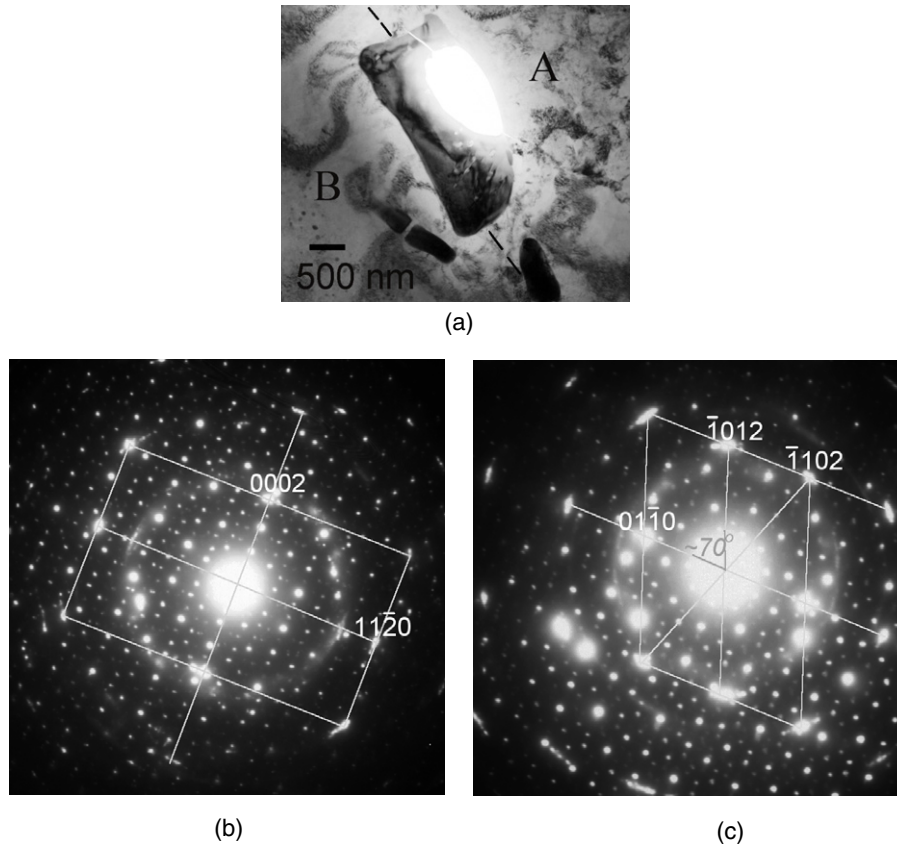
The powder x-ray diffraction patterns of the icosahedral phase are characterized by two very intense peaks corresponding to the most intense diffraction spot  $\{211111\}$  along the fivefold direction, followed by  $\{221001\}$  spot along the twofold direction. These indices are  $\{422222\}$  and  $\{442002\}$ , respectively, in the case of ordered icosahedral phases such as Al–Cu–Fe and Zn–Mg–RE described here. Most of the Al–Cu–TM and Zn–Mg–RE quasicrystals show a pentagonal dodecahedral morphology, indicating that the lowest energy planes are fivefold, twofold and threefold, in that order. Orientation relationships of icosahedral phases with crystalline phases occur in such a way as to match the fivefold and twofold planes with the close packed planes in the crystalline phase. In all the stereograms in this article, traces of fivefold and twofold

planes are shown in dark gray and black, respectively. Fivefold, threefold and twofold axes are marked by appropriate symbols. In addition, the  $\langle \tau 10 \rangle$  type of zone axis is marked by a gray square, in which a fivefold trace crosses a twofold one at  $90^\circ$ . It is also to be noted that in the icosahedral lattice, for any twofold axis there are another two such that all three are mutually perpendicular to each other. Another defining feature in the icosahedral lattice is the angle  $63.4^\circ$  between two fivefold axes/vectors. This matches with the  $60^\circ$  angles common in crystalline lattices.

## 3. Quasicrystal–crystal interfaces

The two main properties of quasicrystals—high rotational symmetry and quasiperiodicity—also play important roles in their interface formation, with crystals, and actually make them easier to form than crystal–crystal interfaces. An example of the effect of high symmetry is in the interface of the icosahedral phase with polycrystalline magnesium [30]. A particle of the icosahedral phase can have crystallographic relationships with two or more grains of  $\alpha$ -Mg which are crystallographically unrelated to each other. Figure 1 illustrates this point. An icosahedral phase occurs at the grain boundary between two grains A and B of  $\alpha$ -Mg. (These micrographs are from a mechanically deformed sample and therefore show strain contrast.) These micrographs/diffraction patterns are taken along the icosahedral phase fivefold zone axis orientation. With respect to this, the corresponding orientations of the grains A and B are shown in the composite diffraction patterns. Grain B is along a  $[1\bar{1}00]$  zone axis of magnesium. It is observed that the hexagonal axis is along a twofold reciprocal vector of the icosahedral phase and the  $(11\bar{2}0)$  vector is perpendicular to it. The  $\alpha$ -Mg phase  $(0002)$  diffraction spot is nearly coincident with the icosahedral  $\{442002\}$  spot along the twofold reciprocal vector. The grain A is along the  $[4\bar{2}\bar{2}3]$  zone axis. It is observed that the geometry of this pattern fits the fivefold diffraction pattern and some prominent reciprocal-space spots coincide. No apparent crystallographic relationship between grain A and B was found, but their relationship to the icosahedral phase seems obvious. Analysis of the orientations showed that these grains are not only in two different orientations with respect to the *i*-phase but also in two different ORs with respect to the *i*-phase. The two grains A and B hold ORs that we will designate as OR1 and OR4 with the *i*-phase, to be discussed in a later section.

We noticed in figure 1 that several diffraction spots of the matrix phase coincide with the prominent diffraction spots of the *i*-phase. This, of course, implies a matching of those planes, but the icosahedral phase is quasiperiodic and therefore there are spots along a particular reciprocal vector which are not simple multiples of each other. This brings us to the second characteristic of quasicrystals—quasiperiodicity. It plays a very important role in the epitaxial relationships with crystals. In the case of crystals, diffraction spots along any reciprocal vector are periodic and therefore give a discrete interplanar spacing. Thus any plane in a periodic crystal can only match another plane of similar spacing in another crystal. In the case of quasiperiodicity, the reciprocal spots along any



**Figure 1.** (a) An icosahedral phase oriented along a fivefold axis showing two kinds of orientation relationships (MgOR1 and MgOR4) with grains (b) B and (c) A shown in (a). Grain B is in  $[1\bar{1}00]$  orientation while A is in  $[4\bar{2}23]$  orientation. (Reproduced with permission from [30]. Copyright 2005, Elsevier.)

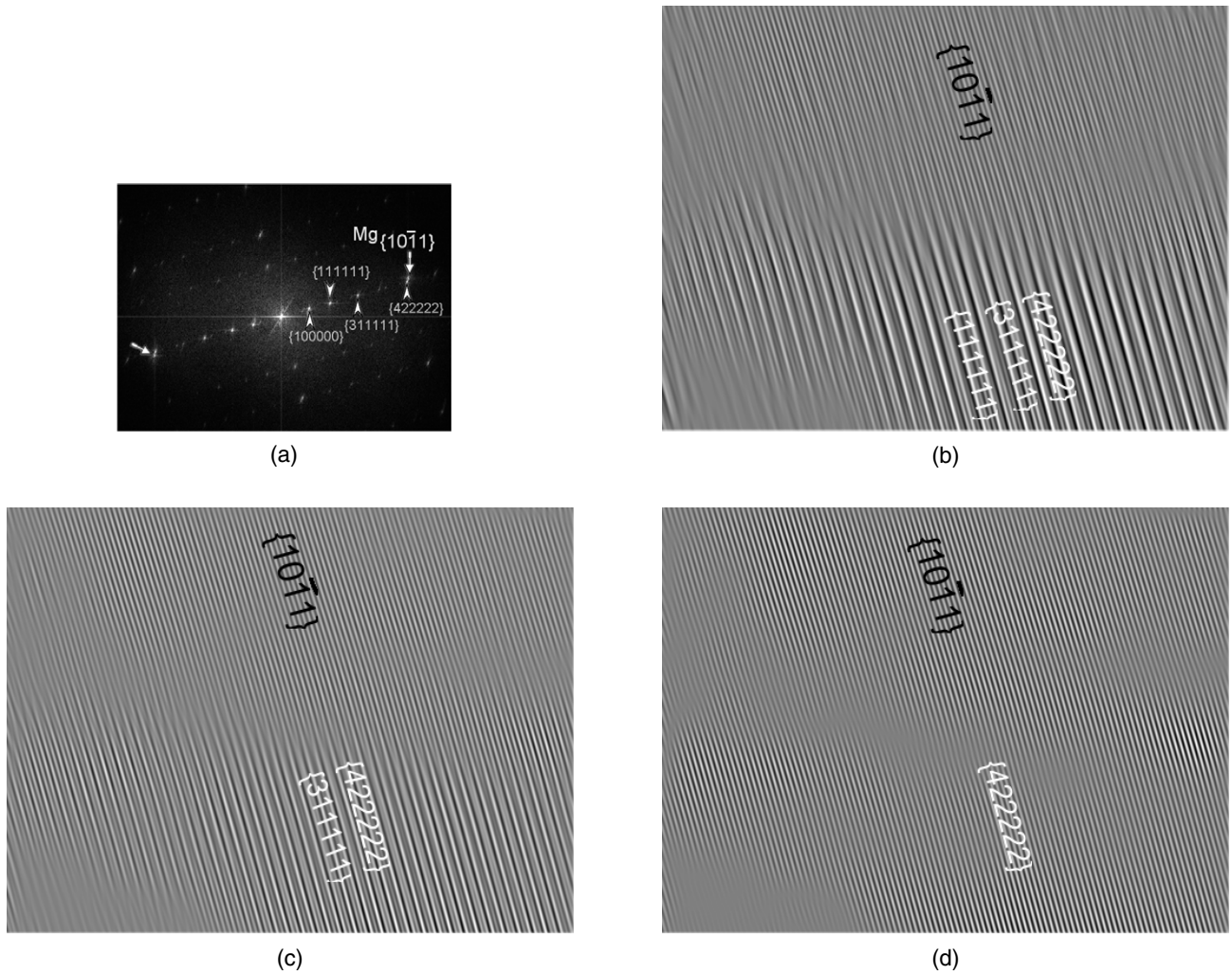
reciprocal vector are quasiperiodic, and therefore generate several interplanar spacings, related to each other by a factor  $\tau$ . Thus a quasiperiodic plane can epitaxially match crystalline planes of several discrete interplanar spacings. This match can be observed in the reciprocal space through the matching of a particular diffraction spot of the quasicrystalline phase with a spot from a crystalline phase. This kind of fit has been called ‘locking into registry’ [22].

Figure 2 is an illustration of an epitaxial relationship. The icosahedral phase is nearly in the orientation of the  $\langle\tau 10\rangle$  zone axis, which shows a fivefold reciprocal vector intersecting a twofold vector at right angles. A fast Fourier transform (FFT) of the high resolution image, figure 2(a), shows spots along a fivefold reciprocal vector and  $\{10\bar{1}\bar{1}\}$  spots from the matrix, which are nearly coincident with the prominent spots  $\{422222\}$ . Figure 2(b) is an inverse Fourier fast transform (IFFT) image with spots along the fivefold vector, including the coincident  $\{10\bar{1}\bar{1}\}$  spots of the matrix. The interface is nearly perpendicular to the parallel planes of the two phases (the interface does not look sharp, in part because it is not exactly parallel to the direction of observation). A match across the interface is observed, even though the planes in the i-phase grain are quasiperiodic. If an image is made only from the coincident spots  $\{10\bar{1}\bar{1}\}$  and  $\{422222\}$ , then we can clearly see a one-to-one match at the interface, for coincidence of the diffraction spots also means equal interplanar spacing, in this case  $\sim 2.4$  Å. If a crystal diffraction spot were

coincident with the  $\{311111\}$  spot, we would see such a match at the interface of  $\sim 2.4/\tau \approx 1.48$  Å. Thus a quasiperiodic plane can accommodate matching of periodic planes of several interplanar spacings across an interface.

In the case of bulk materials we need to know about all possible interfaces formed by a particular orientation of two phases. Stereographic representations are the best way to look at these relationships at a glance, since they give three-dimensional information in one diagram. It must again be kept in mind that here we are dealing with relationships in which one part is crystalline and the other is quasicrystalline. Therefore, a perfect angular match cannot be maintained at all interfaces (even in best possible ORs) as between any two crystals. As to which set of planes would exhibit a perfect match, that would depend on at which surface the nucleation of the phase occurs. On other interfaces only approximate angular matches are expected. Even with a few degrees of misalignment, though, an epitaxial relationship still occurs at the interface.

Figure 3 illustrates this point, in which the interface of an icosahedral phase with magnesium matrix in a Mg–Zn–Y alloy is shown. There are two sets of  $\{10\bar{1}\bar{1}\}$  ( $\sim 2.45$  Å) planes, one matching with the intense fivefold spot  $\{422222\}$  (2.35 Å) and another with the twofold  $\{442002\}$  spot (2.43 Å). The Fourier filtered image in (c) shows a match of the  $\{422222\}$  planes with  $(1\bar{1}01)$ , in which the directions of the matching planes differ only by about  $2^\circ$ . Just two dislocation-like features are



**Figure 2.** Effect of Fourier filtering for observing the match at interfaces. (a) The spots in a FFT are indexed. Image made with (b) three quasicrystalline spots along a fivefold reciprocal vector, (c) with two spots and (d) with only the  $\{422222\}$  spot.

observed at the interface. In the case of planes  $\{442002\}$  and  $(10\bar{1}1)$ , the angular mismatch is over  $7^\circ$ ; discontinuities across the interface are observed in some regions, but a continuous match is observed in other regions (figure 3(e)). Figures 3(d) and (f) show how the interface looks when quasicrystalline components are added to the icosahedral planes.

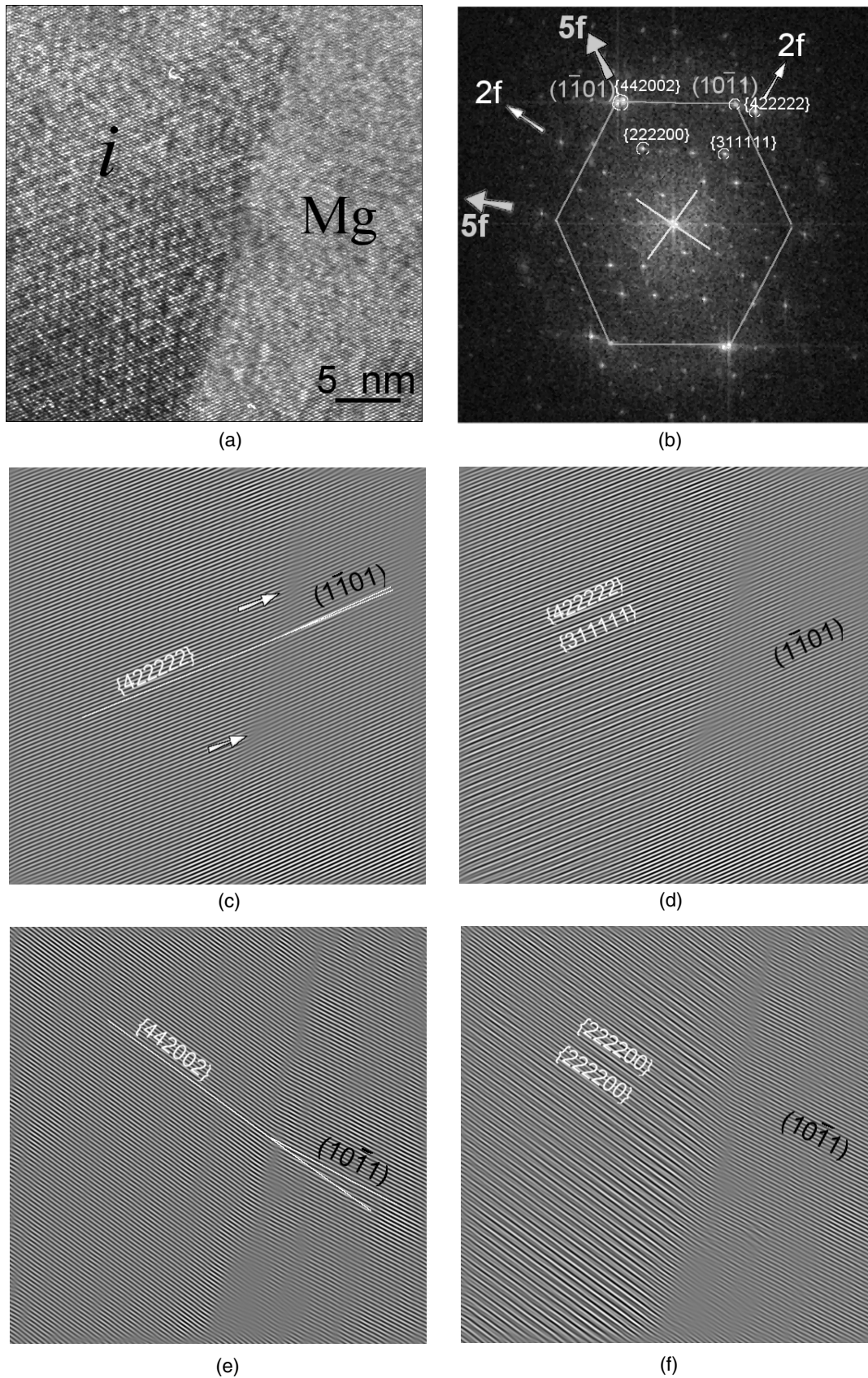
This brings us to another question. In the case of crystal–crystal interfaces, a misfit parameter is defined from the difference in interplanar spacings of the matching planes. Dislocations at regular distances on the interface occur to adjust the misfit. It would be difficult to define misfit dislocations on quasicrystalline planes. Misfit of the crystalline plane with respect to the nearest matching quasicrystalline plane spacing, as illustrated in figures 2 and 3, will be mentioned here.

Epitaxial relationships can thus be determined from composite electron diffractions from two phases, in combination with imaging of the interfaces to determine their direction. The epitaxy at the interfaces can then be confirmed by high resolution or lattice imaging in transmission electron microscopy. In a particular sample, only a few of the interfaces can be observed. To determine the others, we can use stereographic pro-

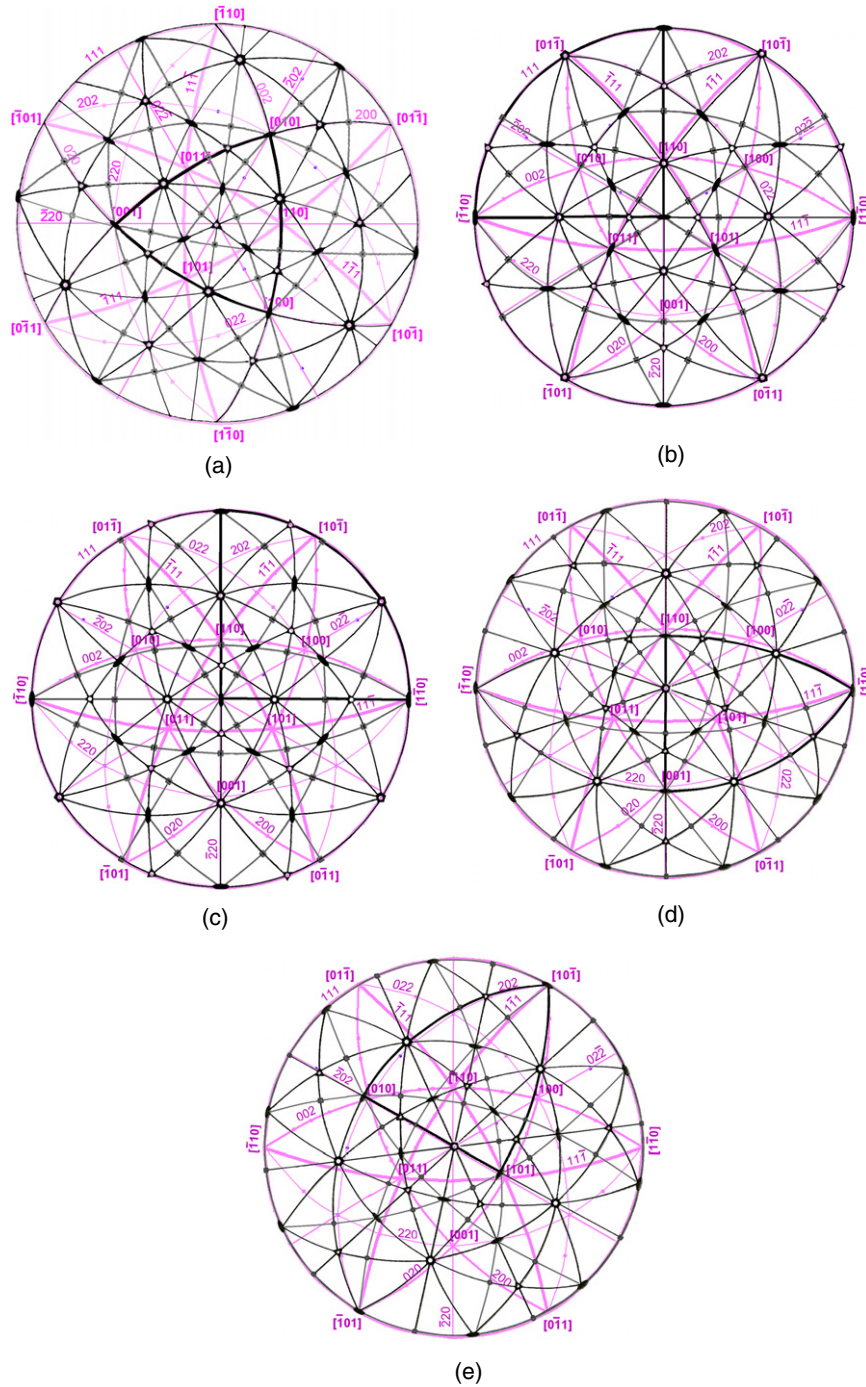
jections. Moreover, the particular interfaces under observation may not be the best fit ones in the case of quasicrystal–crystals. A stereographic projection would show on which planes the best fit occurs.

#### 4. Interfaces of lead particles embedded in an icosahedral phase matrix

We studied lead particles embedded in an Al–Cu–Fe matrix [12–14]. Lead is immiscible in aluminum, copper and iron and thus does not form any compounds in this system. Lead particles were embedded in the alloy by rapid solidification from the liquid state. Three ORs between the lead particles and the icosahedral matrix were reported [13]. Table 1 lists all possible orientation relationships reported thus far, between cubic crystals and icosahedral quasicrystals. These ORs are represented by stereograms in figure 4. In these stereograms, traces of the close packed planes of a face centered cubic phase,  $\{111\}$ ,  $\{200\}$  and  $\{220\}$ , are shown. All the stereograms are orientated with a cubic threefold  $(111)$  axis in the center. In the first OR, called COR1, one of the threefold axes in each phase coincides with another (in the center of the stereogram of figure 4(a)). The most important point is



**Figure 3.** Interface between the i-phase and magnesium. (a) A high resolution TEM image and (b) its FFT showing that the i-phase is oriented along a twofold axis while the matrix is along the  $[2\bar{1}13]$  axis. (c) A Fourier filtered image showing the match between the i-phase  $\{422222\}$  fivefold plane (arrows mark dislocations at the interface) and  $(1\bar{1}01)$ . (d) Same image with two quasiperiodic spots along the fivefold plane. (e) Match of  $\{442002\}$  twofold plane and  $(10\bar{1}1)$ . (f) The filtered image with two quasiperiodic reciprocal spots along the twofold reciprocal vector.

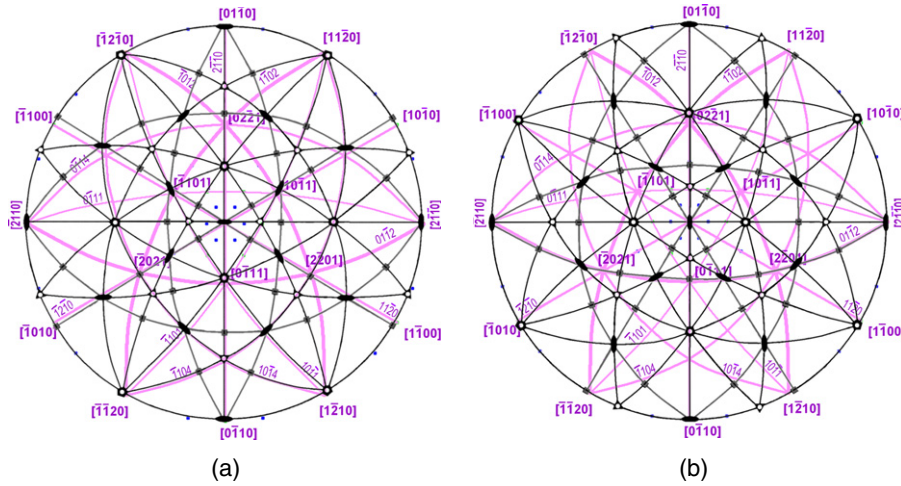


**Figure 4.** Stereographic representations of ORs of cubic phases with i-phase (a) COR1, (b) COR2, (c) COR3, (d) COR4 and (e) COR5. Traces of fivefold and twofold planes of i-phase and close packed planes of a fcc lattice are drawn.

that the three cubic axes  $\langle 100 \rangle$  coincide with three mutually perpendicular icosahedral twofold axes. Thus all the three cubic  $\{200\}$  planes match with an icosahedral twofold plane. This is a unique OR for an icosahedral phase with its cubic approximants due to icosahedral cluster orientations in them, and can be derived from higher dimensional space [2–4].

A best fit between the two lattices is in COR2 (figure 4(b)), where an icosahedral twofold axis is along a threefold axis of the cubic phase. Three of the fivefold planes match with  $\{220\}$  while the other three match with  $\{113\}$ . Three of the twofold planes match  $\{111\}$  and another three match  $\{220\}$ . Thus all

close packed planes of the cubic phase match with close packed planes of the icosahedral phase. COR3 also has an icosahedral twofold axis along a threefold axis  $\langle 111 \rangle$ , but is related to COR2 by a rotation of  $90^\circ$  around this axis (figure 4(c)). A fivefold plane closely matches with  $\{002\}$  and two others with  $\{112\}$ . There are matches of some twofold axes with one each of  $\{111\}$ ,  $\{\bar{1}10\}$  and  $\{11\bar{2}\}$ . CORs 1 to 3 were reported for lead (as OR3, OR1 and OR2, respectively) [13]. A commonality in all these ORs was reported to be a matching of fivefold  $\{422222\}$  ( $2.1 \text{ \AA}$ ) and twofold  $\{442002\}$  ( $2.0 \text{ \AA}$ ) planes with  $\{220\}$  ( $1.75 \text{ \AA}$ ).



**Figure 5.** Stereographic representations of ORs of bismuth with i-phase (a) BiOR1 and (b) BiOR2. Traces of fivefold and twofold planes of i-phase and close packed planes of bismuth are drawn.

**Table 1.** Matching of planes of cubic phases with i-phase fivefold and twofold planes in the orientation relationships reported.

OR	Icosahedral planes (or axes)	Corresponding cubic planes (or axes)
(1)	Twofold Fivefold (a 3f    {111}) (Cubic rational approximants)	{100}(3), {112}(3), {123}(3) {012}(3)
(2)	Twofold Fivefold (three {τ10}    {100})	{111}(3), {110}(3), {112}(1) {110}(3), {113}(3)
(3)	Twofold Fivefold	{010}(2), {111}(1), {110}(1), {112}(1), {014}(2) {100}(1), {112}(2), {315}(2), ~{122}(1)
(4)	Twofold Fivefold	{001}(1), {110}(2), {112}(4) {111}(2), {112}(2), {113}(2)
(5)	Twofold Fivefold	{110}(1), {112}(4), ~{221}(1) {111}(1), {211}(2)

Two more ORs of cubic phases have been reported in the literature. Both have a fivefold axis along a threefold axis of the cubic phase, related to each other by 90° around this common axis, shown as COR4 and COR5 in figures 4(d) and (e). Thus in both of these cases, a fivefold plane will match a {111} cube plane. In COR4, another fivefold plane is reasonably close to (111̄). Three of the twofold planes are parallel to (002), (220) and (22̄0), which are mutually perpendicular (thus three mutually perpendicular twofold axes are along [001], [110] and [11̄0]). In COR5, another fivefold plane is reasonably close to a (111̄) plane, and a set of three mutually perpendicular twofold planes match with (020), (202) and (2̄02).

### 5. Interfaces of bismuth particles embedded in an icosahedral phase matrix

Bismuth has a rhombohedral unit cell (indexed here in hexagonal coordinates). Like lead, it is immiscible in aluminum, copper or iron in the solid state. There have been studies of bismuth particles embedded in aluminum matrices, which indicate that bismuth does not make good interfaces with aluminum. In the OR reported [31, 32], there is a match of one of the closest packed planes {011̄2} of bismuth with a {111} plane of aluminum. This OR, however, leaves other close packed planes of both the phases unmatched. Therefore,

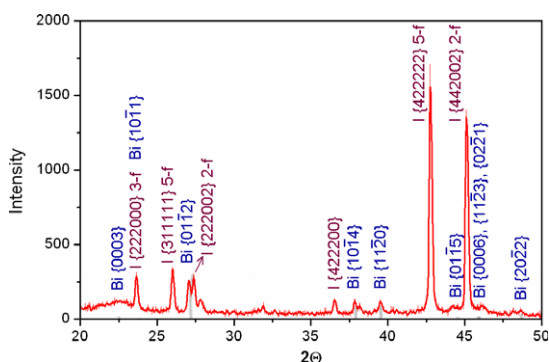
except for one parallel type of sharp interface, the interfaces are disordered. This is manifest in a lowering of the melting temperature of bismuth nanoparticles when embedded in an aluminum matrix. We embedded bismuth particles in an icosahedral phase matrix of Al–Cu–Fe and showed that there is no change of melting temperature of bismuth particles [15]. It was shown that bismuth lattice has a better fit with the icosahedral matrix than with any crystalline one [33].

Figure 5(a) shows the stereogram of an OR called BiOR1, between bismuth and the icosahedral phase. The trigonal axis of bismuth is along an icosahedral twofold axis. Traces of bismuth close packed planes {011̄2}, {112̄0}, {011̄1} and {101̄4} are drawn. The planar matches are listed in table 2. A match of nearly all these planes with a twofold or a fivefold plane is observed in the stereogram. There is a match of all prominent zone axes too, as is readily observed. To consider epitaxy, a powder x-ray diffraction pattern of the composite material is shown in figure 6. Peaks close to the most prominent peaks of the icosahedral phase, fivefold {422222} and twofold {442002}, are {101̄4}, {112̄0}, {011̄5}, {0006}, {112̄3}, {0221} and {2022}. All of these bismuth planes have a match in BiOR1 with either {422222} or {442002} planes. These epitaxial matches are listed in table 2. It should be mentioned that {112̄0}, {101̄4} and {2022} planes are



**Table 2.** Epitaxial matching between i-phase and bismuth planes in BiOR1.

Bismuth planes			Icosahedral phase planes		Mismatch (%)
Indices	Numbers	Spacing (Å)	Indices	Spacing (Å)	
Match with fivefold planes			Fivefold		
$\bar{2}113$	2	1.97	{422222}	2.1	-6.19
$01\bar{1}5$	1	2.03	{422222}	2.1	-3.33
$0\bar{2}01$	1	0.95	{844444}	1.05	-9.52
$11\bar{2}0$	2	2.27	{422222}	2.1	8.09
Match with twofold planes			Twofold		
0003	1	3.95	{221001}	4.0	-1.25
$03\bar{3}0$	1	1.31	{664004}	1.24	5.64
$2\bar{1}\bar{1}0$	1	2.27	{442002}	2.0	13.5
$10\bar{1}1$	2	3.74	{221001}	4.0	-6.5
$\bar{3}033$	2	1.25	{664004}	1.24	0.81
$10\bar{1}4$	2	2.37	{332002}	2.6	-8.85
$\bar{3}0312$	2	0.80	{10106006}	0.77	3.9
$12\bar{3}5$	2	1.26	{664004}	1.24	1.61
$2537$	2	0.80	{10106006}	0.77	3.9



**Figure 6.** X-ray powder diffraction pattern of bismuth particles embedded in Al-Cu-Fe i-phase.

second, third and fourth most intense peaks, respectively, in the bismuth powder diffraction pattern<sup>4</sup>. Electron diffraction and lattice image evidence of these matches are shown in [33].

Figure 7 shows the epitaxial match at interfaces of a particle of bismuth with a modification of BiOR1. The icosahedral matrix is in a  $\langle \tau 10 \rangle$  zone axis orientation, showing a five and a twofold plane, at right angles to each other. In the bismuth particle, these planes are matched with  $(\bar{2}11\bar{3})$  and  $(02\bar{2}1)$  planes, respectively. The match of the fivefold plane is as expected in BiOR1, but that of  $\{02\bar{2}1\}$  with an icosahedral twofold plane is a modification (as can be expected between a quasicrystal and a crystal) replacing  $\{03\bar{3}0\}$ . The angle between these two planes of bismuth is about  $82.5^\circ$ . In the Fourier filtered image, the match at the interface is seen clearly. The match of the  $\{02\bar{2}1\}$  spots with  $\{442002\}$  spots is perfect, as observed in the FFT.

In BiOR1, however, the most intense bismuth peak  $\{01\bar{1}2\}$  does not find a match with a prominent plane of the icosahedral phase. Thus an alternative OR is possible. This OR, a variant of BiOR1 by a rotation of  $90^\circ$ , is shown on a stereogram in figure 5(b). A fivefold trace is observed to match with the  $\{01\bar{1}2\}$  plane. Thus there is a match of a set of the closest

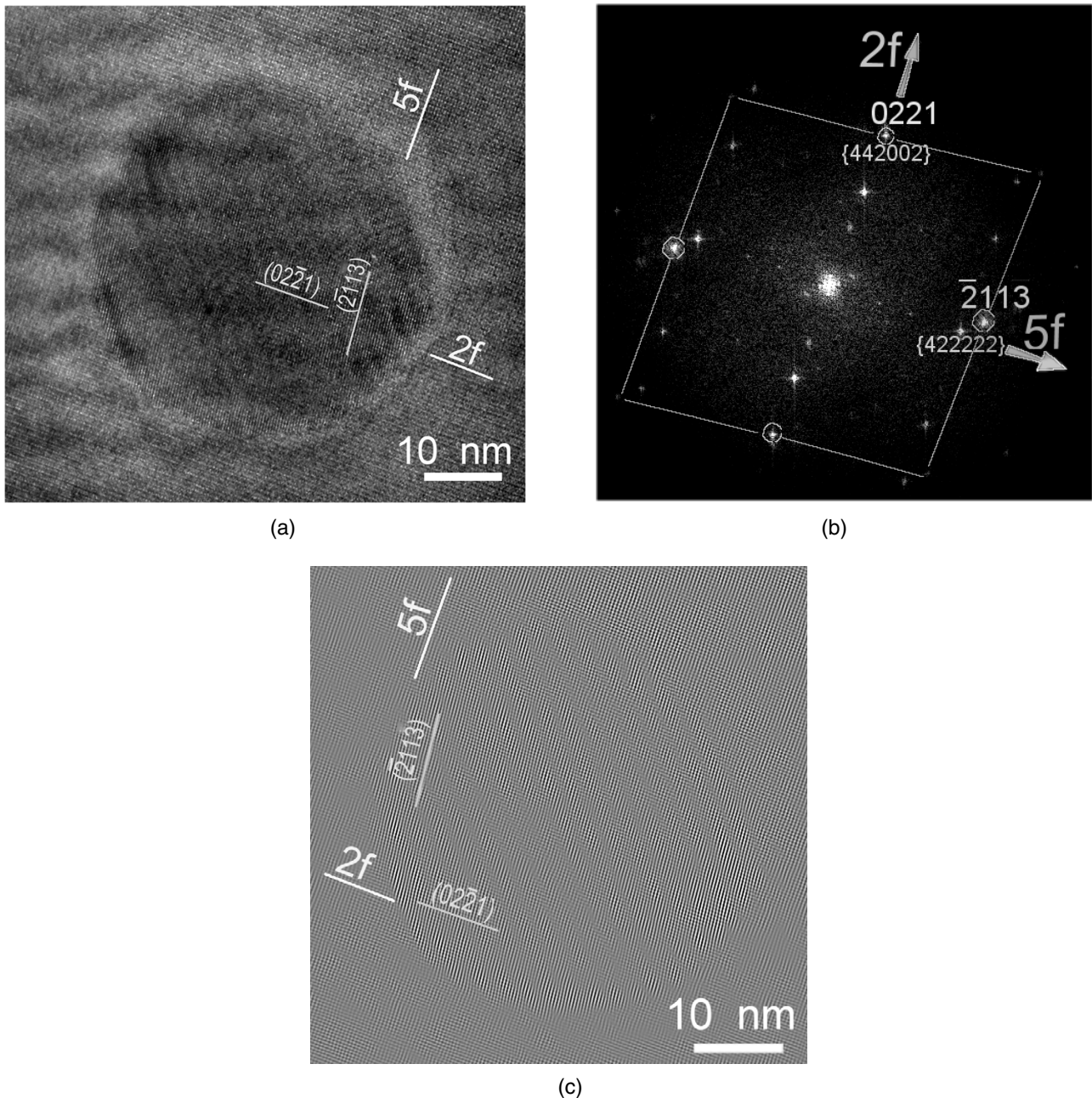
packed planes in both the phases. In addition, the other two  $\{01\bar{1}2\}$  planes are angularly close to two twofold planes. To consider epitaxy it should be noted in figure 6 that the  $\{01\bar{1}2\}$  peak is close to (and in between) a fivefold peak  $\{311111\}$  and a twofold peak  $\{222002\}$ , which are  $\tau$  deflections of  $\{422222\}$  and  $\{442002\}$ , respectively. BiOR2 was demonstrated in [33]. With the icosahedral matrix along a diamond zone axis, a bismuth particle occurred with its  $[2201]$  axis about  $7^\circ$  away. This is a modification of BiOR2 by a few degrees of rotation such that both the fivefold and the twofold planes in this zone match two  $\{01\bar{1}2\}$  bismuth planes uniformly. Thus two  $\{01\bar{1}2\}$  planes of bismuth will have an epitaxial match with a fivefold  $\{311111\}$  and with a twofold  $\{222002\}$  plane of the icosahedral phase.

## 6. Interfaces of tin particles embedded in an icosahedral phase matrix

Elemental tin is immiscible in aluminum in the solid state, but forms compounds with copper and iron. However, when tin is embedded into an Al-Cu-Fe alloy of stoichiometric composition of icosahedral phase, the icosahedral phase and tin separate out. Tin is tetragonal in structure. Annealing at higher temperatures to get a phason defect-free icosahedral phase results in a rapid growth of the tin particles [16, 17]. These particles are sharply faceted.

The tin ( $\beta$ ) unit cell is tetragonal. Several ORs with the icosahedral matrix were found. The close packed planes of tin are  $\{200\}$ ,  $\{101\}$ ,  $\{211\}$  and  $\{110\}$ , in that order, whose traces are drawn in the stereogram in figure 8. Figures 8(a)–(c) show a tin particle, its diffraction with the matrix and the stereographic representation. The matrix is in fivefold orientation while the tin particle is along  $[010]$ . It is observed in the composite diffraction pattern that an icosahedral twofold vector coincides with the tin  $c$ -vector. The  $\{444004\}$  twofold plane (1.6 Å) matches the  $(002)$  Sn plane (1.6 Å). The  $(200)$  spot (2.9 Å) matches a spot  $\{20\bar{1}100\}$  (2.75 Å) along another important icosahedral vector which exists in between two twofold vectors. The two  $\{101\}$  vectors in this diffraction

<sup>4</sup> Powder diffraction, file No 44-1246 JSPDF.



**Figure 7.** (a) Lattice image of a bismuth particle embedded in Al–Cu–Fe i-phase matrix; the bismuth particle is in the  $[4\bar{3}14]$  zone axis containing  $(2113)$  and  $(0221)$  planes and the i-phase is in a  $\langle \tau 10 \rangle$  zone axis containing fivefold and twofold vectors at  $90^\circ$ , as shown in the FFT (b). (c) A Fourier filtered image with only the matching planes. A slight overlap of the phases produced moiré fringes.

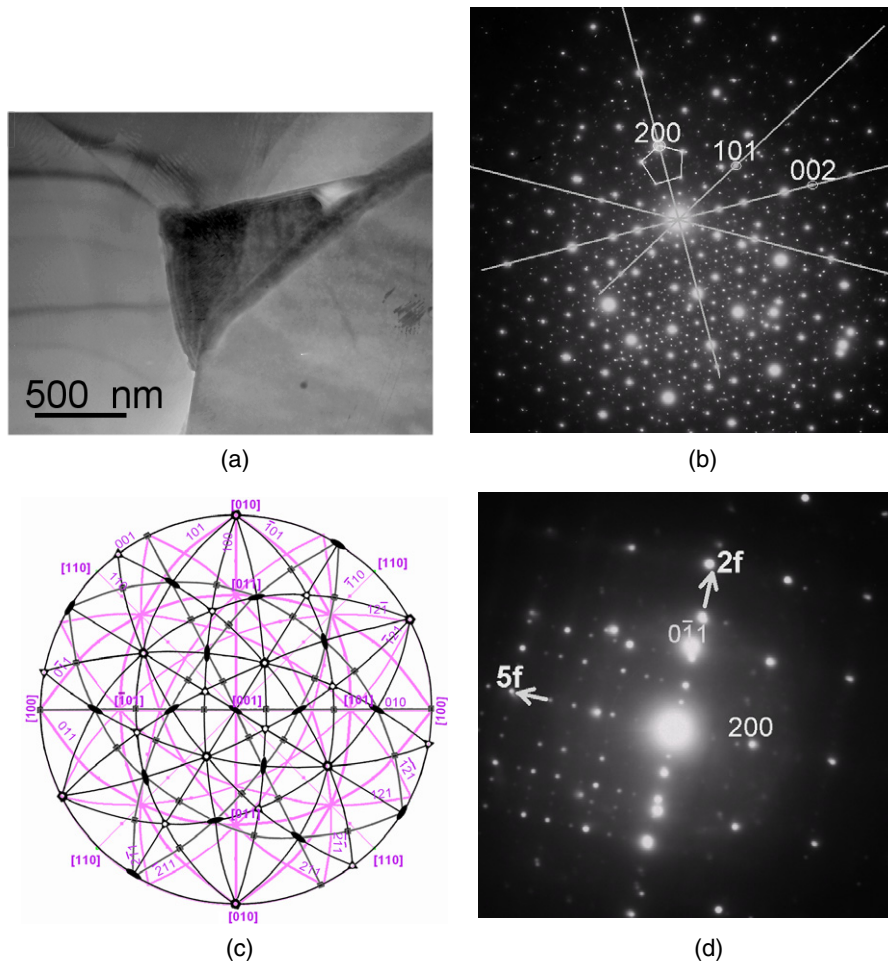
pattern are close to two icosahedral twofold vectors. The corresponding bright field image of the tin particles shows that two planar facets at right angles to each other are oriented such as to be on tin  $(200)$  and  $(002)$  planes. Thus an epitaxial match of close packed planes will occur on these facets. The stereogram reveals that the most prominent planar match in this OR is between a fivefold and  $(020)$ , which are the closest packed in both the phases.

Another OR is shown in a diffraction pattern in figure 8(d). The matrix is in a  $\langle \tau 10 \rangle$  zone while the tin particle is along the  $[011]$  zone axis. The  $(0\bar{1}1)$  plane ( $2.79 \text{ \AA}$ ) is parallel to the twofold plane  $\{222002\}$  ( $3.24 \text{ \AA}$ ), while the  $(200)$  plane is parallel to a fivefold plane. The spacing of the  $(400)$  plane

( $1.45 \text{ \AA}$ ) is close to  $\{733333\}$  ( $1.3 \text{ \AA}$ ). Thus there is a match of the two most densely packed planes in the respective phases.

### 7. Interfaces of icosahedral phase particles in magnesium matrix

An important application of icosahedral quasicrystal, not expected earlier among the possible major applications, is in strengthening magnesium alloys for structural applications, in which the strong interface with the magnesium matrix plays a very important role. Magnesium is hexagonal, with a nearly ideal  $c/a$  axial ratio. An orientation relationship exists between hexagonal phases structurally related to quasicrystals and the



**Figure 8.** (a) A tin particle embedded in Al–Cu–Fe *i*-phase, (b) the corresponding composite diffraction pattern showing the *i*-phase in a fivefold zone axis orientation and the tin particle along its [010] axis, and (c) the corresponding OR shown on a stereogram. (d) A diffraction pattern from another tin particle where the matrix is in  $\langle\tau 10\rangle$  orientation while the particle is along [011].

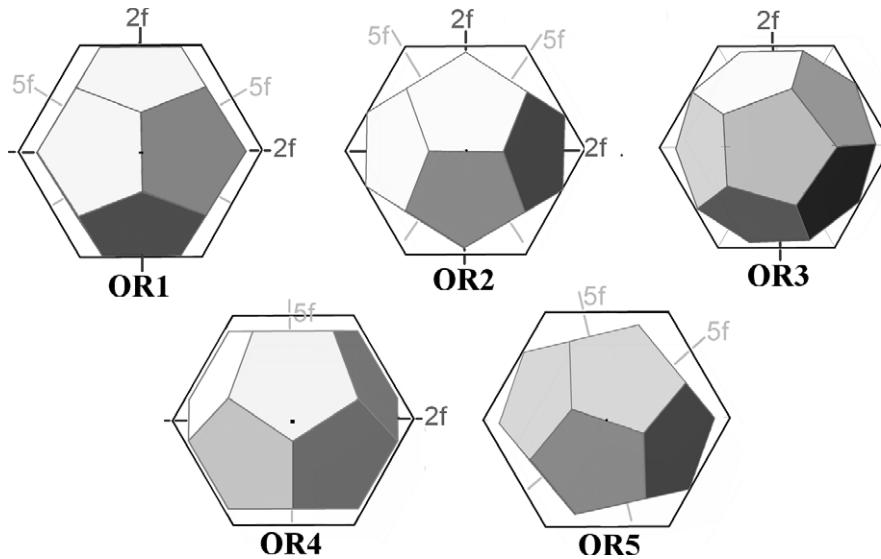
icosahedral phase [34–36] in which an icosahedral twofold axis occurs along the hexagonal axis in a symmetrical fashion, with another two twofold axes along twofold axes of the hexagonal phase. Magnesium also shows this OR with the *i*-phase [37]. Since magnesium has a simple structure not related to the icosahedral phase, it shows other ORs too [38].

The close packed planes in the magnesium lattice are  $\{10\bar{1}1\}$ ,  $\{0002\}$  and  $\{10\bar{1}0\}$ , in that order. The ORs of *i*-phase with magnesium are represented with hexagons and pentagonal dodecahedra in figure 9. The hexagons represent magnesium unit cells looking down its *c*-axis, and the dodecahedra, which are truncated icosahedra with pentagonal faces, are oriented with respect to the hexagons to show the mutual orientations. In three of the ORs an icosahedral twofold axis is along the hexagonal axis. Of these, MgOR1 is similar to the OR observed between the *i*-phase and the quasicrystal-related hexagonal phases. A set of prismatic planes match twofold planes, and the other two prismatic planes match fivefold planes. A set of  $\{11\bar{2}0\}$  planes match icosahedral twofold planes. Further matches are listed in table 3. MgOR2 is a variant of MgOR1, related by a rotation of  $90^\circ$  around the coincident axis. In this, two fivefold planes match  $\{11\bar{2}0\}$  planes, while a twofold plane matches a set of prismatic planes.

This OR also exhibits a good match between prominent planes. Interfaces are formed on these prominent matching planes. The planar epitaxial matches with the icosahedral lattice are shown for MgOR1 and MgOR2 in table 3.

In another OR, MgOR3, a fivefold plane exists parallel to the hexagonal basal plane. A set of twofold planes match a set of prismatic planes. It has been shown that these three ORs can be derived from each other by considering the common  $\{10\bar{1}2\}$  twins in magnesium [38]. Two more ORs have been shown to exist in magnesium alloys. In MgOR4 a  $\langle\tau 10\rangle$  zone axis occurs along the hexagonal axis. In this OR, one of the fivefold planes matches a prismatic plane, and a twofold plane matches a  $\{11\bar{2}0\}$  plane. In MgOR5 an icosahedral twofold axis is parallel to the hexagonal axis, but asymmetrically.

In Mg–Zn–Y alloys MgOR1 was observed most commonly, followed by MgOR2 and the obscure looking MgOR4. MgOR3 has been observed in a cast Mg–Zn–Ho alloy. In these ORs, the morphology of the *i*-phase is often plate-like in the basal plane of the Mg matrix. Just as MgOR1 and MgOR2 are variants of each other related by  $90^\circ$ , such variants of other ORs occur too. Figure 10 is an example of the variant of MgOR4. The *i*-phase particle in a sample annealed at high temperatures is viewed along a twofold axis



**Figure 9.** The five ORs of i-phase in a magnesium matrix. Hexagons represent orientation of the magnesium lattice along its hexagonal axis and the pentagonal dodecahedra show the corresponding orientation of the i-phase. MgOR2 (OR2) is a 90° variant of MgOR1 (OR1). Such variants also exist for MgOR3 (OR3), MgOR4 (OR4) and MgOR5 (OR5).

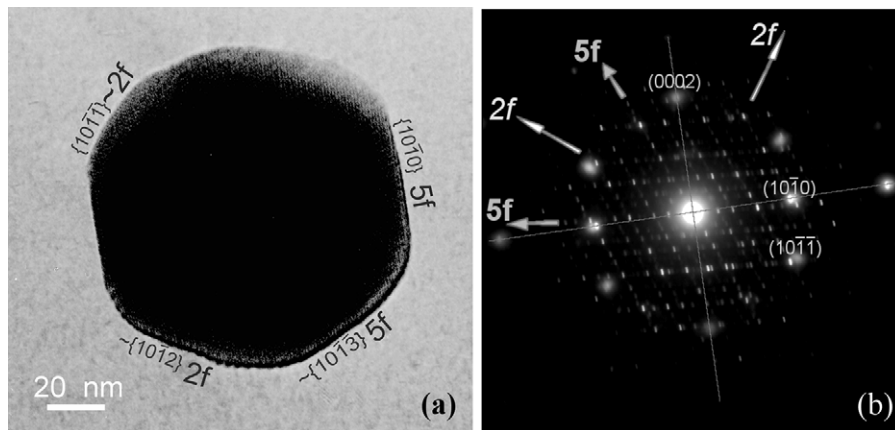
**Table 3.** Epitaxial matching between i-phases and the magnesium matrix in orientation relationships OR1 and OR2.

Magnesium planes		Icosahedral planes		Mismatch (%)
Indices (No)	Spacing (Å)	Indices	Spacing (Å)	
<b>OR1:</b>				
Match with fivefold planes		Fivefold planes		
{011} (2)	2.45	{422222}	2.435	-0.61
{100} (2)	2.778	{422222}	2.435	-12.35
{216}(2)	0.762	{14 6 6 6 6 6}	0.75	-1.57
Match with twofold planes		Twofold planes		
{001}	2.605	{442002}	2.34	-10.17
{100} (2)	2.778	{442002}	2.34	-15.77
{111} (4)	1.54	{664004}/τ	1.446	-6.10
{116} (4)	0.762	{12 12 8 0 0 8}	0.723	-5.12
{101} (4)	2.45	{442002}	2.34	-4.49
<b>OR2:</b>				
Match with fivefold planes		Fivefold planes		
{013} (2)	1.473	{733333}	1.5	1.83
{21̄2}(2)	1.3664	{733333}	1.5	9.78
{110} (2)	1.6047	{733333}	1.5	-6.52
Match with twofold planes		Twofold planes		
{001}	2.605	{442002}	2.34	-10.17
{010}	2.778	{442002}	2.34	-15.77
{21̄0}	1.6	{664004}	1.446	-9.63
{123} (4)	0.8988	{10 10 6 0 0 6}	0.894	-0.53
{503} (4)	1.06	{10 10 6 0 0 6}	0.894	-15.66
~{103}(4)	1.473	{664004}	1.446	-1.83

while the matrix is along the  $[01\bar{1}0]^*$  axis. The particle is sharply faceted but not on the basal plane because no major icosahedral symmetry plane matches the matrix basal plane. It is faceted on its fivefold and twofold planes. The sharpest facet is one on which a fivefold  $\{422222\}$  plane matches a  $(10\bar{1}0)$  prismatic plane. Another two long but rougher facets are found on which a fivefold plane roughly matches a  $\{10\bar{1}\bar{3}\}$  plane and on which a twofold plane roughly matches a  $\{10\bar{1}2\}$  plane. A short face on which a good epitaxial match should occur is of a twofold  $\{422002\}$  plane matching a  $\{10\bar{1}\bar{1}\}$  plane.

### 8. Discussion

Even though the i-phase is quasiperiodic, it can form epitaxial interfaces easily in bulk materials. The quasiperiodicity contributes very significantly to this. The high symmetry facilitates the formation of matching interfaces by providing favorable orientations. Both of these properties—high symmetry and quasiperiodicity—contribute to forming epitaxy on all the interfaces in the bulk. This leads to important properties in bulk materials such as significant enhancement



**Figure 10.** A particle of i-phase in magnesium matrix showing MgOR4' (a 90° variant of MgOR4) (a) and the corresponding composite diffraction pattern in which the i-phase is oriented along a twofold zone axis while the matrix is oriented along a [1210] axis.

of strength and ductility as in magnesium alloys containing quasicrystals [18–20] or enhancement of melting temperature as in bismuth embedded in an i-phase matrix [15, 33]. Strengthening intermetallic phases in a metal matrix usually have a low symmetry, so that a part of their interface is non-coherent, reducing the ductility of the material. The i-phase can form all coherent interfaces.

It is also significant to note that bismuth makes very good interfaces with the i-phase but not with any crystalline phase. When embedded in an aluminum matrix, a set of closest packed planes in the two phases match to form a sharp interface, leaving the rest of the interfaces disordered [31, 32]. For this reason, bismuth particles embedded in an aluminum matrix show a reduction of the melting temperature [31, 32]. For embedding in an i-phase matrix, there is no reduction of the melting temperature [15] and all the interfaces are faceted [33].

## 9. Conclusions

Formation of interfaces of crystalline lead, bismuth, tin and magnesium with the i-phase in bulk has been studied. These elements show several orientation relationships with the i-phase, forming epitaxy on all the interfaces with matching close packed planes. The high symmetry of the i-phase provides favorable orientation and the quasiperiodicity provides possibilities for epitaxial matching at the interfaces. These properties open up possibilities for fabrication of bulk materials and devices with phenomenal properties.

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