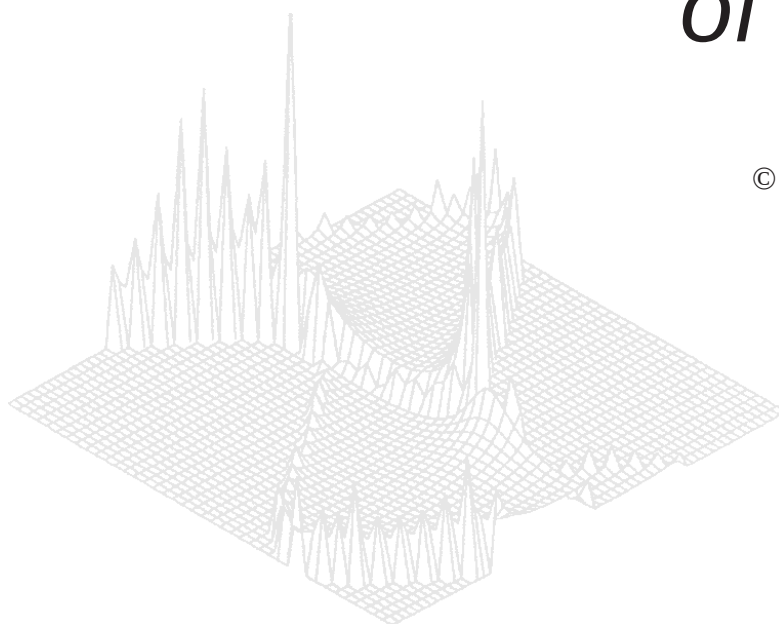

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HRTEM Study of α -AlMnSi Crystals including Non-crystallographic Projection Axes

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Abstract

The structure of α -AlMnSi is examined by atomic resolution high-resolution transmission electron microscopy (HRTEM) and computer-based image matching techniques. Six distinct zone axes are examined; including both normal crystallographic and non-crystallographic zone axes of the structural motifs, which have $m\bar{3}5$ icosahedral symmetry. The results provide a sound basis for understanding HRTEM images of crystalline and quasicrystalline alloys of AlMnSi; thus we examine to what extent the requirements for obtaining so-called structure images of complex alloy structures may be met experimentally and define when the images may be reliably interpreted on the basis of computer simulation and image-matching at about 0.17 nm resolution. Most difficulty was experienced in obtaining the experimental images, especially for the non-crystallographic zones, which are very sensitive to slight changes in orientation off the desired zone axis or projection, the rate at which the crystal thickness is increasing (wedge-angle) and the orientation of the surfaces of the specimen. Surface amorphous layers due to oxidation and/or electron-induced irradiation damage also limit the efficiency of the HRTEM analysis.

For the thin specimens used for HRTEM, both the electron diffraction patterns and the HRTEM images are characteristic of $Im\bar{3}$ space group symmetry. It is suggested that this $Im\bar{3}$ symmetry may be an example of a statistical symmetry, where the local symmetry is close to $Pm\bar{3}$ but the average symmetry is $Im\bar{3}$. The transition from $Pm\bar{3}$ to $Im\bar{3}$ may be understood in terms of an analysis of small changes in the outer shells of the large icosahedral structural elements which are located at the corners and body-centres of the cubic unit cell.

1. Introduction

Linus Pauling (1985) raised some questions concerning the interpretation of diffraction data from quasicrystals. The most fundamental question concerns the limits to our ability to distinguish between a true quasicrystal (e.g. as specified by a Penrose tiling) and periodic crystals, sometimes including multiply-twinned variations of alloy structures, with large complex unit cells. The latter have become known as approximants (Goldman and Kelton 1993). For example, Yang (1988) surveyed the structural studies of the α -AlMnSi phase and applied the method of projection from six-dimensional space to give an idealised model for the structure of the α phase assuming the building blocks were related to the Mackay icosahedron (MI) and the double Mackay icosahedron (DMI); his work implied a close relationship between the crystalline and icosahedral quasicrystalline phases. In fact, structural similarities between known crystalline phases, such

as α -AlMnSi and related quasicrystalline phases such as i-AlMnSi, have been explored in some detail by many authors since 1985; see Bursill and Peng (1985) for an early study and Goldman and Kelton (1993) for a recent review.

We expect that crystalline approximants other than α -AlMnSi (see Goldman and Kelton 1993) may become more readily identifiable following a careful study of the HRTEM images, as well as electron diffraction patterns, of the α phase and its corresponding quasicrystalline alloys. In particular this paper is concerned with HRTEM images of the α phase viewed along the 2-, 3- and 5-fold axes of the icosahedral building units. Thus atomic resolution images of both crystallographic and non-crystallographic zone axes are studied, both experimentally as well as theoretically. We expect that this approach will finally allow us to obtain an improved understanding of the structure of the quasicrystalline phases and their approximants.

The results of an electron diffraction study of α -AlMnSi have also been reported (Song and Bursill 1997a); it was shown that this phase undergoes an order-disorder structural phase transition from $Pm\bar{3}$ towards $Im\bar{3}$ space group symmetry for very thin specimens.

The present paper includes high-resolution transmission electron microscopic results for crystalline α -AlMnSi, which demonstrate some details of the structural properties of α -AlMnSi, especially its similarity to the quasicrystalline phase when it is viewed along non-crystallographic directions like $[0\tau 1]$.

2. Experimental

α -AlMnSi crystals with an approximate formula of $(Al, Si)_{0.83}Mn_{0.17}$ (cf. Cooper and Robinson 1966) were prepared from high purity starting materials (Al 99.99%, Mn 99.98% and Si 99.9999%) by mixing 62.5wt.% Al, 27.5wt.% Mn and 10.0wt.% Si in an alumina crucible and sintering in a furnace under Argon protection; firstly at 1200°C for two hours to produce an homogeneous liquid phase, then at about 660°C for twelve hours to make the α phase. The result appeared to be crystalline needles with shortest dimension of about 0.1–0.2 mm. Larger single crystals were obtained by recrystallising in a vacuum furnace at 900°C, then slowly cooling at about 3° per hour. Some single crystals of about 0.3–0.5 mm diameter were obtained in this way.

Specimens suitable for transmission electron microscopy and electron diffraction studies were obtained by crushing the α -AlMnSi crystal fragments under ethanol with a mortar and pestle, preparing a suspension and then depositing a drop of the latter onto a holey carbon film supported by a 400 mesh copper grid.

The high-resolution images were obtained with a JEOL-4000EX high-resolution electron microscope operating at an accelerating voltage of 400 kV. This instrument was equipped with a top-entry goniometer having tilt capability of $\pm 20^\circ$ about two orthogonal axes. It has a point to point resolution limit of 1.7 Å and allows accelerating voltages of up to 400 kV to be used. Electron diffraction patterns were also obtained using the JEOL-4000EX in the course of the high-resolution work.

Optical transforms of the HRTEM images were produced using an optical diffractometer equipped with a He-Ne laser. The patterns were recorded on Polaroid film.

Table 1. Atomic coordinates for α -AlMnSi and α -AlFeSi in symmetries of $Pm\bar{3}$ and $Im\bar{3}$ based on the data of x-ray experiments

Note that the $Im\bar{3}$ structure requires a random mixture of two types of cell; Al(3), Al(6) and Al(7) are occupied in cell I whereas Al(3a), Al(6a) and Al(7a) are occupied in cell II; physically the two sets of sites are related by a translation of half a body diagonal

	Symmetry	Symmetry	Pm $\bar{3}$ /Im $\bar{3}$ cell I			Im $\bar{3}$ cell II		
	Pm $\bar{3}$	Im $\bar{3}$	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
Mn/Fe(1)	12j	24g	0.3243	0.1981	0	0.3243	0.1981	0
Mn/Fe(2)	12k	(24g)	0.1757	0.3019	0.5	0.1757	0.3019	0.5
Al(1)	6e	12d	0.3777	0	0	0.3777	0	0
Al(2)	6h	(12d)	0.1223	0.5	0.5	0.1223	0.5	0.5
Al(3)	6f	12e	0.2990	0	0.5	—	—	—
Al(3a)	6g	(12e)	—	—	—	0.2010	0.5	0
Al(4)	12j	24g	0.1651	0.1006	0	0.1651	0.1006	0
Al(5)	12k	(24g)	0.3349	0.3994	0.5	0.3349	0.3994	0.5
Al(6)	12j	24g	0.3266	0.4030	0	—	—	—
Al(6a)	12k	(24g)	—	—	—	0.1734	0.0970	0.5
Al(7)	12k	24g	0.1275	0.1170	0.5	—	—	—
Al(7a)	12j	(24g)	—	—	—	0.3725	0.3830	0
Al(8)	24l	48h	0.1146	0.1872	0.3003	0.1146	0.1872	0.3003
Al(9)	24l	(48h)	0.3854	0.3128	0.1997	0.3854	0.3128	0.1997

3. Structure of α -AlMnSi

Table 1 lists crystallographic data for α -AlMnSi ($Pm\bar{3}$; Cooper and Robinson 1966) and for α -AlFeSi ($Im\bar{3}$; Cooper 1967). We first describe the $Pm\bar{3}$ structure. (In the following we will refer to the golden mean τ which is defined by the equation $\tau + 1 = \tau^2$; thus τ is an irrational number with value ≈ 1.618 .)

Fig. 1 shows 2-, 3- and 5-fold projections of successive shells about the origin (vertices) of the unit cell (see Cooper and Robinson 1966; Fowler *et al.* 1988; Tibballs *et al.* 1989 for some original structural descriptions). Starting at a corner of the unit cell, there is an inner shell of twelve atoms Al(4) lying at the vertices of the icosahedron of radius $r = 0.1816a_0$ (Figs 1*a, b, c*). Table 2 lists the distribution of crystallographic sites over the first four shells of atoms having approximately icosahedral symmetry.

Figs 1*d, e, f* show icosahedra obtained by adding 12 Mn atoms radially outside the first shell of Al atoms. The completed second shell (Figs 1*g, h, i*) contains forty-two atoms—twelve Mn(1), six Al(1) and twenty-four Al(8). The twelve Mn atoms form a normal icosahedron which has radius twice that of the first shell, with $r = 0.3632a_0$. The six Al(1) atoms lie on the perpendicular bisectors of six of the edges of the triangular faces of this Mn icosahedron; i.e. the six such edges which lie parallel to the (001) surfaces of the unit cell. These six Al(1) atoms lie at a radial distance of $0.3820a_0$ from the origin of the unit cell, which is just $2/\sqrt{\tau^2 + 1} = 1/\cos 18^\circ \approx 1.051$ times the distance of the Mn atoms. The twenty-four Al(8) atoms occupy the remaining similar positions just outside the edges of the Mn(1) icosahedron. Icosahedral symmetry is retained to this stage.

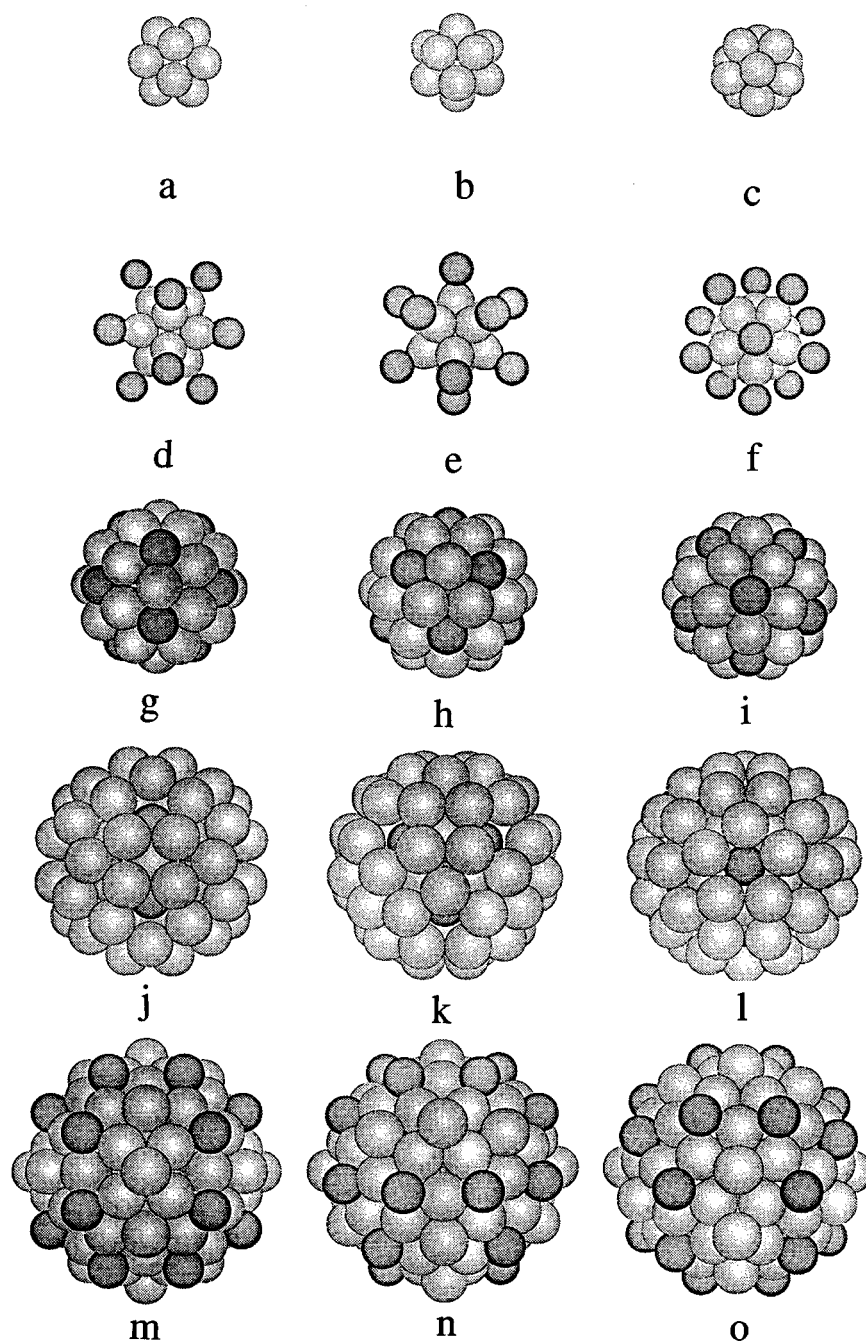


Fig. 1. The 2-, 3- and 5-fold projections of successive shells about the origin (vertices) of the unit cell. Mn atoms are indicated by dark rings. Note that icosahedral symmetry is retained for the third shell but is lost at the fourth shell.

Table 2. Polyhedral shells for α -AlMnSi ($Pm\bar{3}$)

Atomic type numbers in the parentheses refer to those in Table 1. Specific symmetry axis types are indicated next, if applicable. The last value for each atom type is the shell radii with respect to the centre of the polyhedron in terms of the unit cell parameters a_0

Polyhedra at corner					Polyhedra at body centre			
	Atom	Multip.	Symmetry	Radius	Atom	Multip.	Symmetry	Radius
Shell 1	Al(4)	12	5f	$0.1816a_0$	Al(5)	12	5f	$0.1816a_0$
Shell 2	Mn(1)	12	5f	$0.3632a_0$	Mn(2)	12	5f	$0.3632a_0$
	Al(1)	6	2f	$0.3820a_0$	Al(2)	6	2f	$0.3820a_0$
	Al(8)	24	2f	$0.3820a_0$	Al(9)	24	2f	$0.3820a_0$
Shell 3	Al(6)	12		$0.5271a_0$				
	Al(7)	24		$0.5271a_0$				
	Al(9)	24		$0.5271a_0$				
Shell 4	Al(3)	12	5f	$0.5878a_0$				
	Al(1)*	6	2f	$0.6180a_0$				
	Mn(2)	24	2f	$0.6180a_0$				

The third shell (Figs 1*j, k, l*) contains 60 atoms at the vertices of a $60(5434)^*$ polyhedron with 62 faces, including 12 pentagons, 20 triangles and 30 squares. It contains twelve Al(6) atoms, twenty-four Al(7) atoms and twenty-four Al(9) atoms. The twenty-four Al(7) atoms form six squares parallel to the surfaces of the unit cell. The twenty-four Al(9) atoms form eight regular triangles perpendicular to the $[111]$ directions and are shared with the outershell of the adjacent MI at the body centre. The twelve Al(6) atoms, together with the twenty-four Al(7) atoms, form twelve regular triangles other than those in $[111]$ directions.

The fourth shell is an icosahedron self-similar to the second shell but $\tau = 1.618...$ times in diameter (Figs 1*m, n, o*). It contains forty-two atoms, i.e. twelve Al(3) and twenty-four Mn(2) which are shared with the outer shell of the MI at the body centre and six Al(1) atoms which are outside the unit cell and shared by the outer shell of the MI at the corners of the neighbouring unit cells. The twelve Al(3) atoms lie on the vertices of a normal icosahedron with $r = 0.5878a_0$. The Al(1) and Mn(2) lie on the equivalent position as do the Al(1) and Al(8) in the second shell. The total number of atoms associated with the DMI is $12 + 42 + 60 + 42 = 156$.

The structure of the MI at the body centre is exactly the same as the first two shells of the DMI but with the atoms replaced by their counterparts around the body centre. Al(5) replaces Al(4), Mn(2) replaces Mn(1), Al(2) replaces Al(1) and Al(9) replaces Al(8). The whole structure has $Pm\bar{3}$ symmetry according to the above description. Finally, one may fill space completely as represented in Fig. 2, which shows $2 \times 2 \times 2$ unit cells.

The structure of the $Im\bar{3}$ phase appears to differ essentially only in the distribution of the Al and Si atoms over some of the sites. Table 3 gives details of the distribution of the atomic sites over the four shells, assuming the structure is isostructural with AlFeSi (Cooper 1967; Tibballs 1990). Further discussion of the structural transformation between $Pm\bar{3}$ and $Im\bar{3}$ structures is given in the discussion section below.

* $M(N_1^{k_1} N_2^{k_2} \dots N_i^{k_i})$ means that a polyhedron consists of M vertices and each vertex is surrounded by k_i polygons with N_i edges.

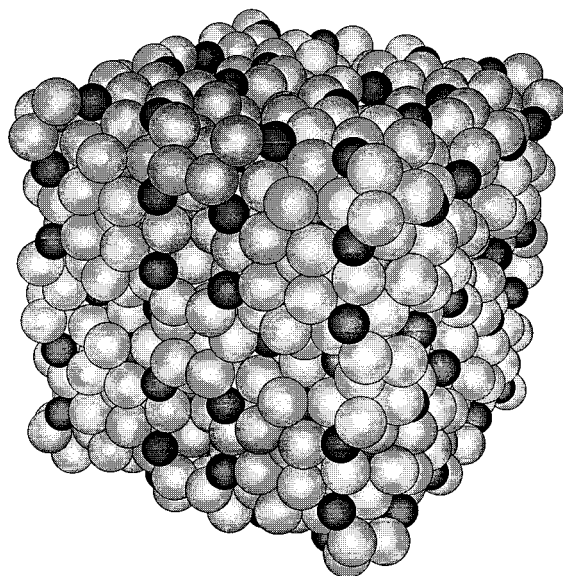


Fig. 2. Space-filling of α -AlMnSi for 2×2 unit cells; Mn atoms are indicated by smaller, dark balls.

Table 3. Polyhedral shells for α -AlMnSi ($\text{Im}\bar{3}$)

Atomic type numbers in the parentheses refer to those in Table 1. Specific symmetry axis types are indicated next, if applicable. The last value for each atom type is the shell radii with respect to the centre of the polyhedron in terms of the unit cell parameters a_0

Polyhedra at corner					Polyhedra at body centre			
	Atom	Multip.	Symmetry	Radius	Atom	Multip.	Symmetry	Radius
Shell 1	Al(4)	12	5f	$0.1816a_0$	Al(5)	12	5f	$0.1816a_0$
Shell 2	Mn(1)	12	5f	$0.3632a_0$	Mn(2)	12	5f	$0.3632a_0$
	Al(1)	6	2f	$0.3820a_0$	Al(2)	6	2f	$0.3820a_0$
	Al(8)	24	2f	$0.3820a_0$	Al(9)	24	2f	$0.3820a_0$
Shell 3	Al(6)	12		$0.5271a_0$	Al(6a)	12		$0.5271a_0$
	Al(7)	24		$0.5271a_0$	Al(7a)	24		$0.5271a_0$
	Al(9)	24		$0.5271a_0$	Al(8)	24		$0.5271a_0$
Shell 4	Al(3)	12	5f	$0.5878a_0$	Al(3a)	12	5f	$0.5878a_0$
	Al(1)*	6	2f	$0.6180a_0$	Al(2)*	6	2f	$0.6180a_0$
	Mn(2)	24	2f	$0.6180a_0$	Mn(1)	24	2f	$0.6180a_0$

4. Computer Simulation of the HRTEM Images

The method used for image simulations of HRTEM images of icosahedral clusters is well documented (see e.g. Barry *et al.* 1985; Peng and Bursill 1990); we are using the software package MEDIS due to Bursill *et al.* (1992) which is an update of MUM (Melbourne University Multislice). The multislice techniques were explained by Goodman and Moodie (1974). Special techniques developed for

some of this work, which allow non-crystallographic zone axes to be calculated, are described in further detail by Song and Bursill (1997b). The unit cell parameter was chosen as $a = 1.268$ nm (Cooper and Robinson 1966). Manganese atoms have a unique set of coordinates in the unit cell whereas aluminium and silicon atoms share another set of coordinates, being statistically distributed with specific occupancy factors determined by the stoichiometry for each of the equivalent 'Al' positions (Tibballs *et al.* 1989). Thus silicon atoms randomly occupy certain aluminium sites (see Tables 1 and 2).

The results of three sets of image simulations for different sets of atomic positions due to Cooper and Robinson (1966), Yang (1988) and Fowler *et al.* (1988) were virtually indistinguishable at 1.7 Å resolution, as may be expected. Similarly, no apparent difference could be recognised in the image simulations using different models for the (Al, Si) occupancies. In order to conserve computing time and storage space, further images were calculated with 100% Al occupancy for (Al, Si) sites using the model of Cooper and Robinson (1966).

Here we give results for the 2-, 3- and 5-fold projection axes of the four shell DMI clusters shown as Figs 1*m, n, o* referred to above. Thus Figs 3*a, b, c* show three structural drawings, alongside the corresponding computer-simulated images, assuming optimum focussing conditions ($\delta f = -450$ Å) which allowed black image intensity to correspond to the projected charge density of the cluster. Note the one-to-one correspondence between atomic positions and the black spots in the images.

Figs 4*a, b, c* are the corresponding atomic projections for crystalline α -AlMnSi for the 2-, 3- and 5-fold axes, together with the corresponding HRTEM images, again assuming the optimum defocus condition for the structure images. In these cases the crystal thickness along the projection axes was chosen equal to 38 Å for Fig. 4*a*, 32 Å for Fig. 4*b* and 34 Å for Fig. 4*c*. It may be seen by close inspection of Figs 4*a–c* that for the case of optimum defocus (≈ -490 Å) and for sufficiently thin specimens, the predicted images do provide a characteristic fingerprint for the α -AlMnSi structure for the 2-, 3- and (pseudo) 5-fold symmetry axes. However, note that incorporation of the MI and DMI into the periodic structure immediately produces significant modification to details of the image contrast of these clusters compared to the corresponding images of isolated clusters; see e.g. the regions closest to the centre and outer ring of the clusters (cf. Figs 3 and 4). An important result is that there is no significant visible difference in image contrast for the projection of DMI and MI, i.e. the corner versus the body-centred positions of the periodic structure, which would allow these two structural units to be located for the 2-, 3- or 5-fold axial projections. Of course this was also true for the corresponding image simulations for $\text{Im}\bar{3}$ which were indeed virtually indistinguishable from the results for $\text{Pm}\bar{3}$. This result is disappointing, since it obviously limits the model sensitiveness of the HRTEM images for analysis of images of the icosahedral phases of α -AlMnSi alloys.

Further discussion of the images predicted for crystalline α -AlMnSi, for a wider range of electron optical conditions is given by Song (1997); in order to conserve space only selected image simulations are included herein, i.e. only those which illustrate image matching conditions for the experimental images reported below.

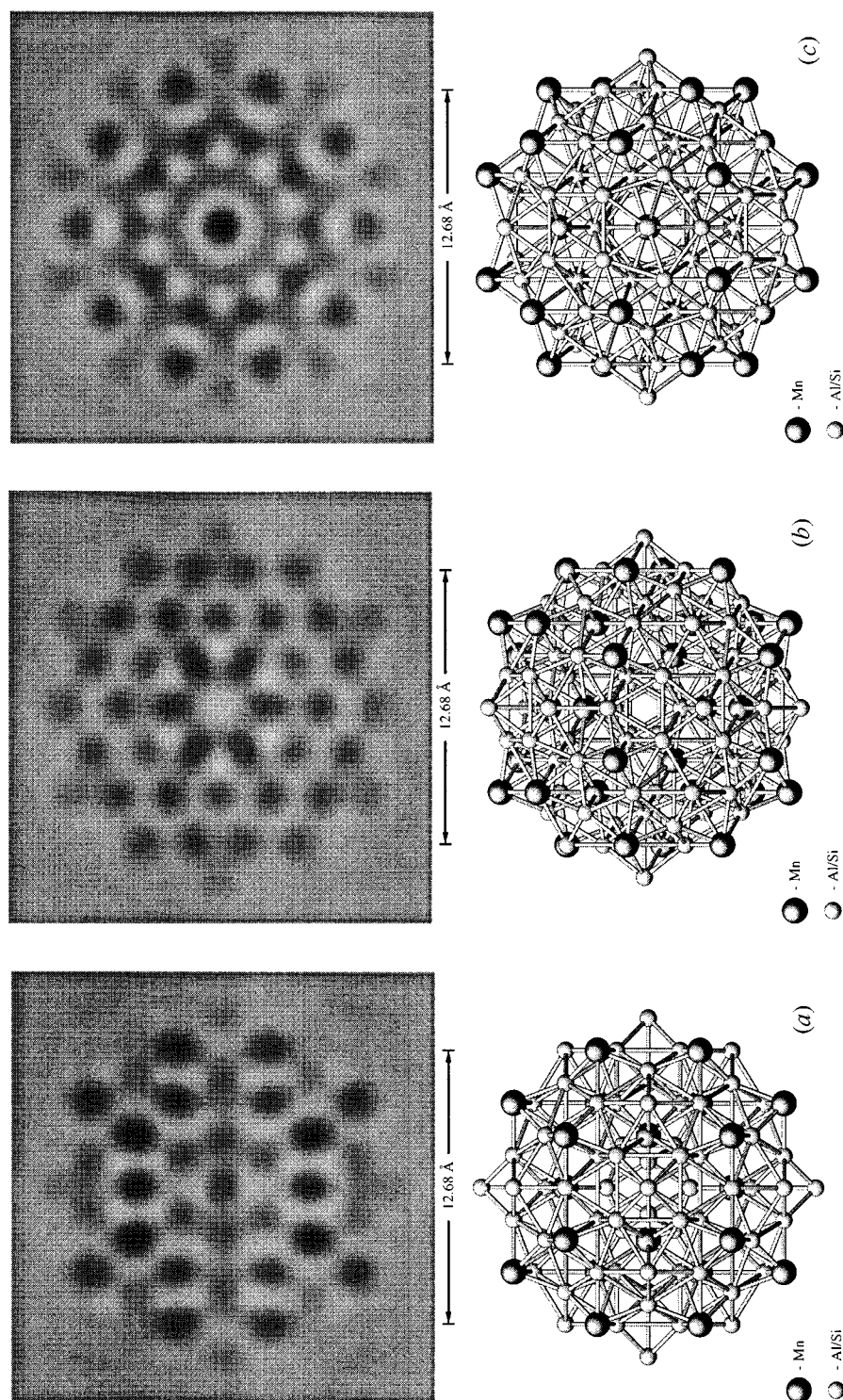


Fig. 3. Parts (a), (b) and (c) show the 2-, 3- and 5-fold projections of DMI clusters of α -AlMnSi, where Mn atoms are indicated by dark rings; the corresponding HRTEM images are for the optimum defocus imaging condition. Note the one-to-one correspondence between atomic density and black spot intensity.

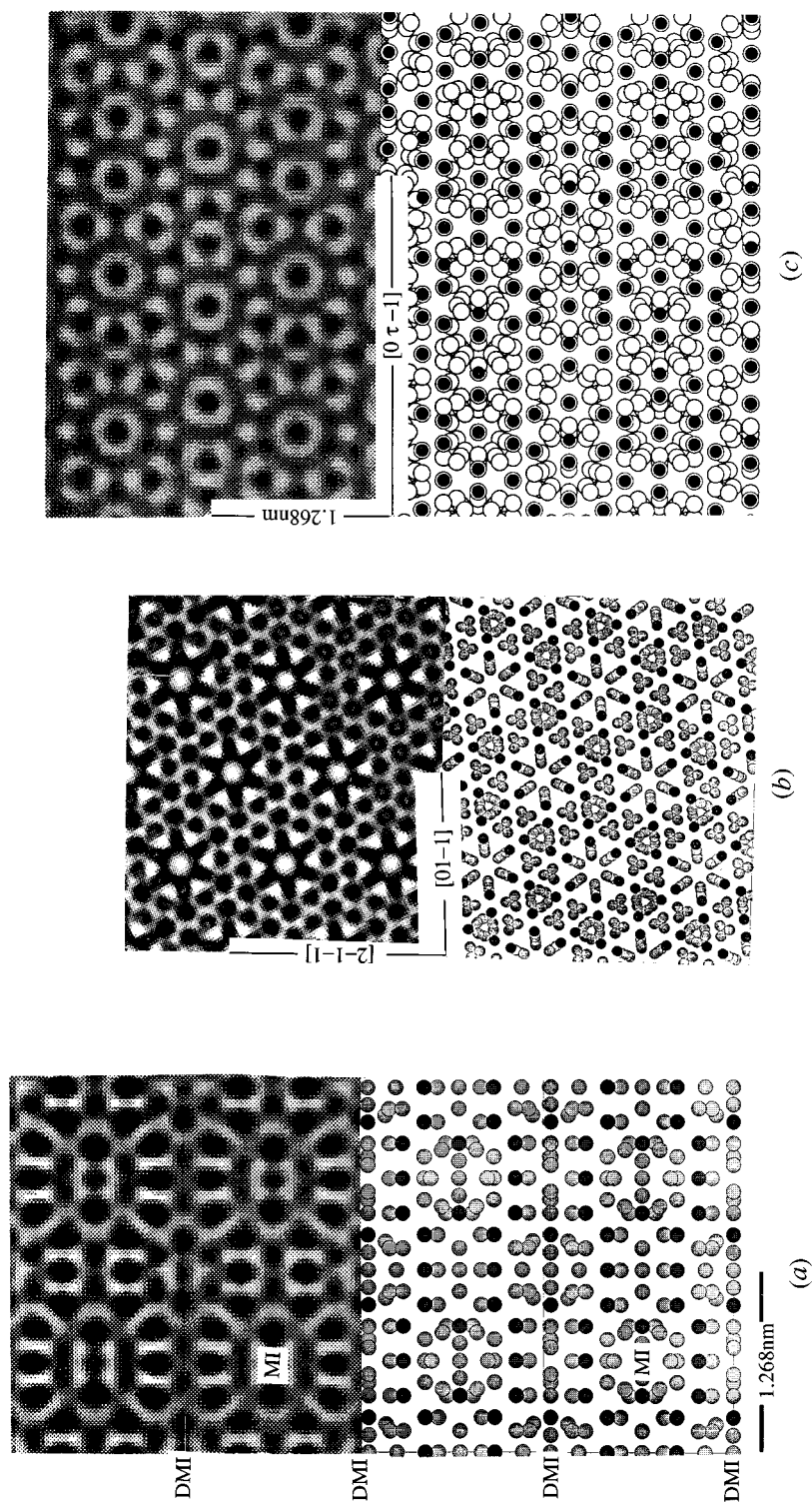


Fig. 4. Parts (a), (b) and (c) show the computer-simulated HRTEM images of crystalline α -AlMnSi for the 2-fold, 3-fold and 5-fold axes, i.e. [001], [111] and [01-1] axes, together with the corresponding structural projections, for the structure image condition.

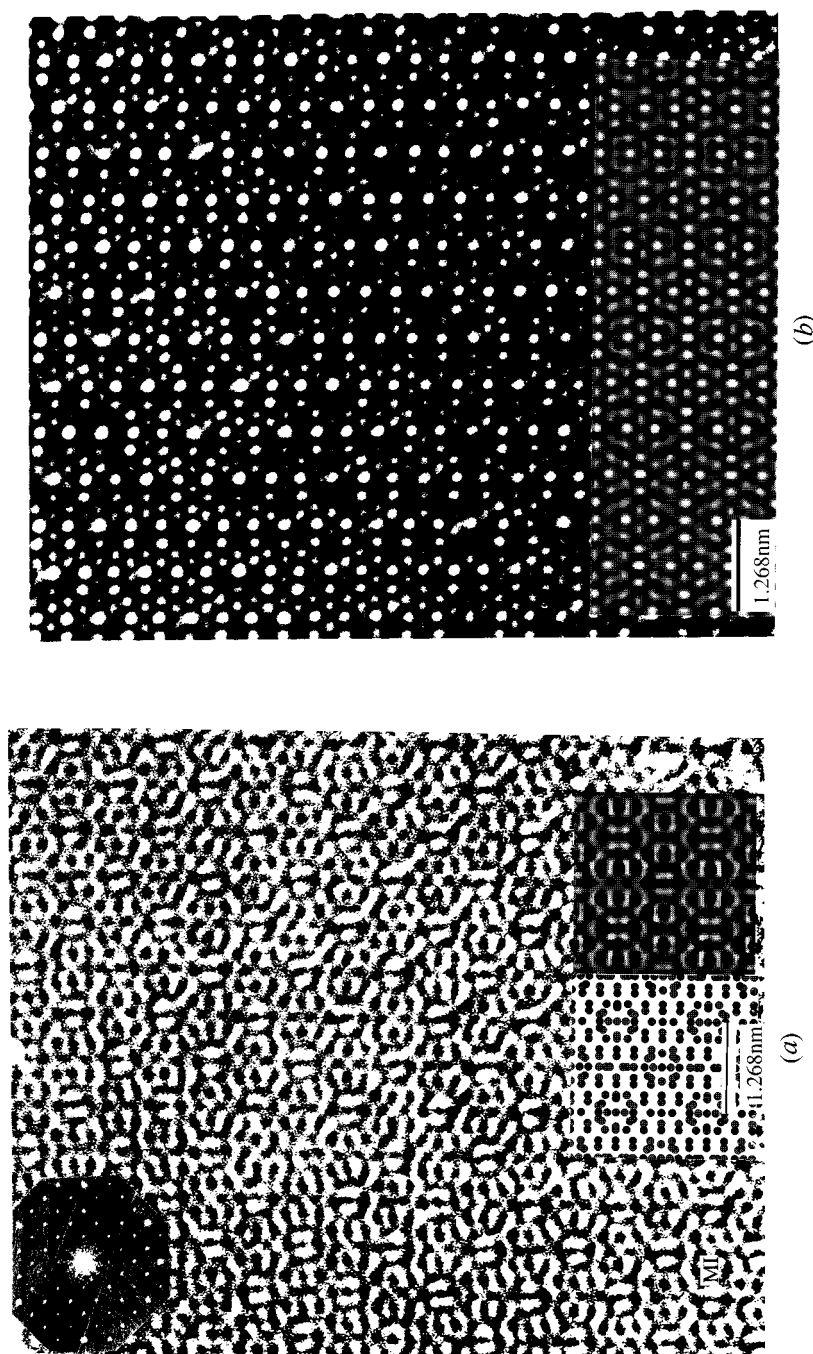


Fig. 5. (a) HRTEM image of the [001] zone axis, cf. Fig. 4a; the optical transform (power spectrum), image match and atomic projection are shown in the insets. (b) HRTEM image of the [001] zone axis, for defocus of -1250 Å. DMI/MI positions may be located by reference to the simulated image and the atomic projection (inset).

5. Results: HRTEM of the α -AlMnSi Crystalline Phase

Figs 5–10 show HRTEM images of α -AlMnSi crystals viewed along various axes, both crystallographic and non-crystallographic. Computer-simulated images matching the experiments, the corresponding atomic projections of the α -AlMnSi structure, as well as optical transforms of the HRTEM images are also included. The HRTEM images and their simulations should be viewed at glancing incidence, in order to reveal more clearly the periodic and aperiodic spacings.

Figs 5*a, b* show two images of the [001] projection; this zone has two-fold symmetry coincident with one of the two-fold axes of the icosahedral units in the unit cell. The two images were obtained for different focus conditions, i.e. -45 nm and -120 nm for (*a*) and (*b*) respectively. Comparison with the structural model of α -AlMnSi for this projection (Fig. 4*a*) and with the shell cluster drawings and their corresponding image simulations (see Fig. 3*a*) does allow the centres of the icosahedral structural units to be located, but it does not allow the DMI clusters to be distinguished from MI. This is because there is no regular apparent difference between the image contrast at corner and body-centre positions (cf. Fig. 4*a*). The optical transform or power spectrum of Fig. 5*a* is shown in the inset. All spots are accounted for assuming space group $\text{Im}\bar{3}$. Thus the projection symmetry of this image implies space group $\text{Im}\bar{3}$ rather than $\text{Pm}\bar{3}$. Close inspection of Fig. 5*b* shows aperiodic fluctuations in the image detail at the corner and body-centred sites of the unit cell.

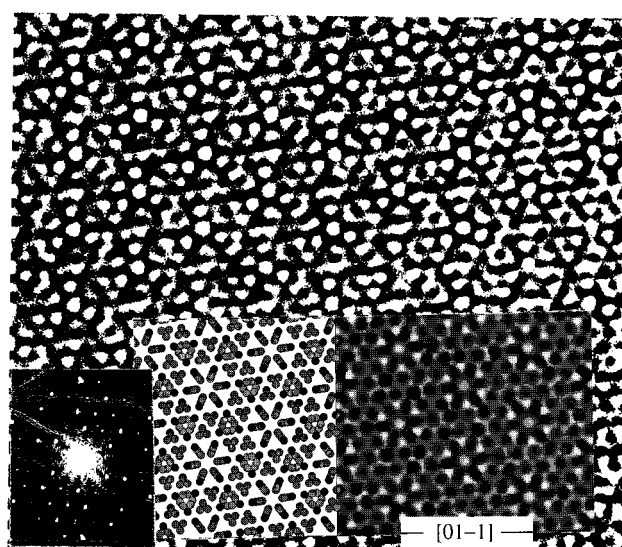


Fig. 6. HRTEM image of the [111] zone axis; the computer-simulated image, structural drawing and power spectrum are inset.

Fig. 6 shows the projection along [111] which is also coincident with one of the three-fold axes of the icosahedra. It can be seen that the triangles of the icosahedron (and the small rhombicosidodecahedron) appear to be rotated from the lattice triangles by 7.8° , as may be anticipated by inspection of the structural drawing and computer simulated image (cf. Fig. 4*b*). The optical transform is

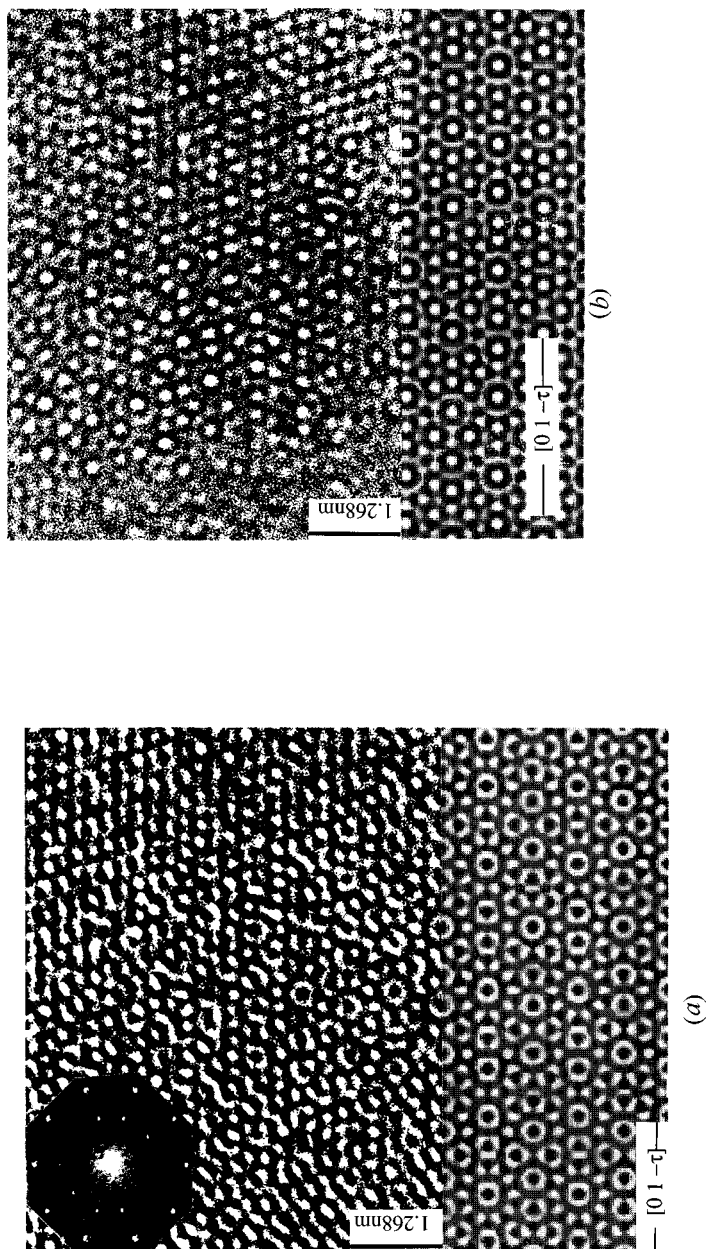


Fig. 7. (a) HRTEM structure image of the $[0\bar{1}1]$ zone axis, cf. Fig. 4c, with objective lens defocus ≈ -490 Å; the power spectrum and image match are inset; (b) same area as (a) for objective lens defocus -700 Å.

inset. This is consistent with both the space groups $\text{Im}\bar{3}$ and $\text{Pm}\bar{3}$, since it is not sensitive to $h + k + l$ odd reflections.

Fig. 7*a* shows the image of a crystal projected along a five-fold axis of the icosahedral structure-building units; this direction may be indexed as $[0\tau 1]$. This is the structure image condition for the $[0\tau 1]$ zone with objective lens defocus of about $-490 \text{ \AA}$. The cube edge is vertical in this image. Fig. 7*b* is the same zone imaged further underfocus (about $-700 \text{ \AA}$). Local five-fold symmetry axes are clearly revealed. The images of these icosahedral units appear to have virtually identical counterparts in HRTEM images of the five-fold axis images of the icosahedral phase (cf. Fig. 1 of Hiraga and Shindo 1990). Note that Fig. 7*a* shows a one-dimensional quasi-lattice with periodicity of a_0 in only one direction (i.e. the crystal direction $[100]$, which runs vertically upwards in this image). The image is aperiodic in other directions. These are probably the first deliberate direct observations of non-crystallographic projections of a periodic crystal, at atomic resolution (i.e. 0.17 nm); thus one is able to obtain one-dimensional quasi-periodicity in a real space image of a periodic crystal. Again, the icosahedral clusters may be located (cf. Figs 3*c*, 4*c*). Note that Fig. 7*a* is a true structure image (black spots image atomic clusters), whereas Fig. 7*b* is not (atomic clusters are centred on the white spots).

Also note that local real space five-fold patterns of Figs 7*a*, *b* are not restricted to lie within one unit cell, but appear to extend to about $2.3a_0$, after which the five-fold symmetry is destroyed by the translational symmetry of the crystal phase. That the tolerance of the crystalline phase to the non-crystallographic icosahedral motif is limited to no greater than about two unit cells is due to an interesting property of the Fibonacci series:

$$1, \tau, 1\tau, \tau 1\tau, 1\tau\tau 1\tau, \tau 1\tau 1\tau\tau 1\tau, \dots$$

Thus periodicity may be tolerated for an extent of about 2 unit cells (e.g. 1, τ , 1, τ), before aperiodicity becomes apparent (e.g. 1, τ , 1, τ , τ , 1, τ).

Fig. 8 shows the images for another three-fold axis of the icosahedra (actually $[01\tau^2]$) which is not equivalent to the crystal zone $[111]$ (cf. Fig. 6 above). It appears in real space to be almost totally periodic, representing faithfully equilateral triangles of manganese atoms. However, the diffraction pattern of this zone reveals its aperiodic properties. The details of the image contrast show the quasiperiodicity along the horizontal direction, especially along the dark lines denoting the corners and body centres of the unit cells.

Fig. 9 is an image of the $[011]$ projection. This is simply a crystallographic zone with a horizontal mirror plane. Note that this projection is not related to the two-fold axis of the DMI and MI structural units. Thus comparison of the structural drawing (inset) and the computer-simulated image (inset) reveals little structural information, despite the impressive image match.

Fig. 10 is an image of the $[1\tau\tau^2]$ projection; close inspection, sighting along different sets of lattice fringes, reveals quasiperiodicities. Note that the horizontal and vertical axis are both aperiodic in this case, although there is a periodic $[11\bar{1}]$ axis in the plane. This is an important image; it reveals the quasi-two-fold axis of the icosahedral units, which is rather similar to the two-fold image found for α -AlMnSi (Hiraga and Shindo 1990). In fact it may easily be mistaken for a

two-fold image of the quasicrystalline phase whereas it is in fact simply a pseudo two-fold image of the crystalline phase.

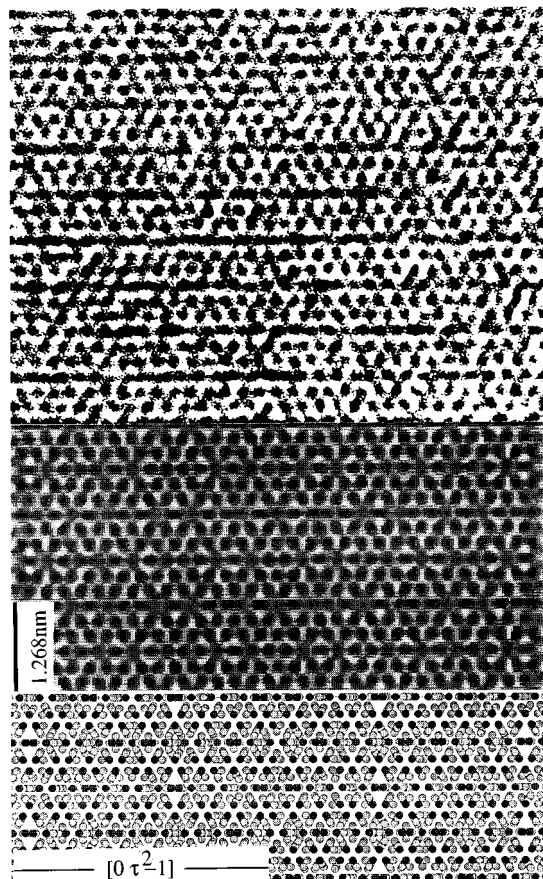


Fig. 8. HRTEM image of the $[01\tau^2]$ zone axis (top) together with the corresponding computer-simulated image and structural drawing for this projection.

Optical diffraction patterns from selected areas are put next to the relevant HRTEM images for most of Figs 5–10 to display the reciprocal space symmetries. The optical transforms can also give local symmetry information, which may be averaged out for electron diffraction patterns. For example, the optical transform of the image of $[0\tau 1]$ (Fig. 7a) shows both periodic and one-dimensional quasiperiodic symmetries for different directions of the five-fold quasicrystal, as does the HRTEM image.

6. Discussion: $Pm\bar{3}$ or $Im\bar{3}$?

For electron diffraction, there are extinction conditions for $Im\bar{3}$ which are quite distinct from those for $Pm\bar{3}$, especially for the $[001]$ zone axis. Thus, for the area shown in Fig. 5a the diffraction pattern had $Im\bar{3}$ symmetry, with systematic

extinction of all reflections with $(h + k + l) = \text{odd}$. These same extinctions apply for the optical transform inset in Fig. 5a.

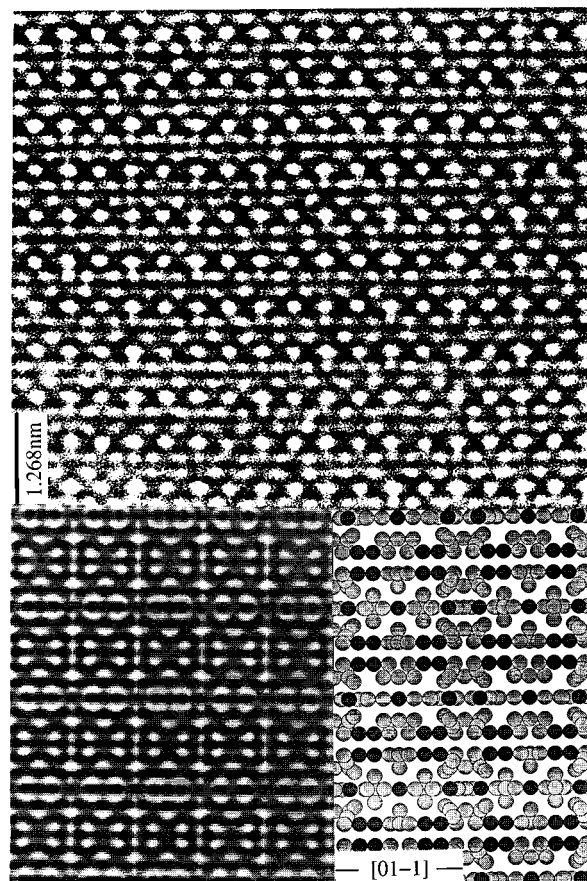


Fig. 9. HRTEM image of the $[011]$ zone axis (top) with the computer-simulated image and structural drawing for this projection.

Some consideration of the crystallography of the space groups $\text{Pm}\bar{3}$ and $\text{Im}\bar{3}$ (see Tables 1–3) shows that these two possibilities should be most readily distinguished for the $[001]$ zone axis images. Essentially, the corner and body-centred sites should, in principle, be distinct for $\text{Pm}\bar{3}$ but identical for $\text{Im}\bar{3}$. However, as shown above, there was in practise no significant difference in image contrast for the corner and body-centred positions of the DMI and MI icosahedral building units of AlMnSi. Close inspection of the $[001]$ zone axis images (Figs 5a, b) shows weak contrast fluctuations at the corners and centres of the unit cell, suggestive of the image simulations predicted for $\text{Pm}\bar{3}$; however, these appear in an aperiodic or disordered fashion, rather than being long-range ordered. Overall the structure of the imaged parts appears statistically equivalent to one with average symmetry $\text{Im}\bar{3}$.

It is concluded that the short-range structure, on the scale of 1.2–3.0 nm, contains the two types of icosahedral clusters, as described by Cooper (1967) and Yang (1988), as expected for space group $Pm\bar{3}$; however, averaging over several unit cells gives apparent symmetry $Im\bar{3}$, at least for the rather thin crystals examined by HRTEM.

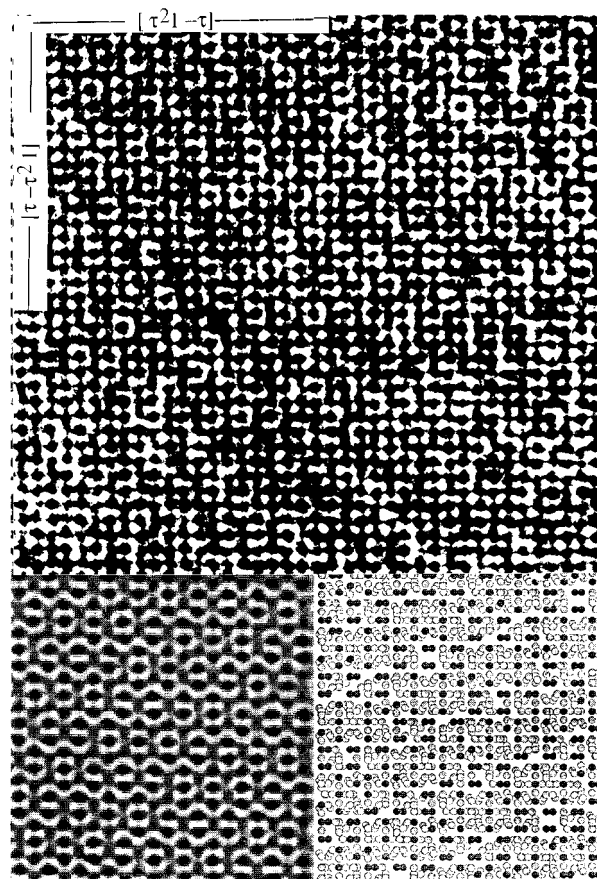


Fig. 10. HRTEM image of the $[1\tau\tau^2]$ zone axis (top) with the computer-simulated image and structural drawing inset.

Note that electron diffraction patterns consistent with $Pm\bar{3}$ symmetry were recorded for this specimen (Song and Bursill 1997a), but only for relatively thick specimens. However, the thin edges required for HRTEM analysis invariably showed only $Im\bar{3}$ reflection conditions. The appearance of $Im\bar{3}$ symmetry, for areas used for HRTEM, may possibly be due to electron bombardment of the thin area, which may cause local rearrangements or disorder, or else there may be a beam-induced structural phase transition in thin films due to electron energy loss processes other than electron–atom knock-on collisions. It is also possible that there may be a real order–disorder transformation from $Pm\bar{3}$ to $Im\bar{3}$ symmetry for thin films, due to altered thermodynamics at the surface of this complex

alloy. Such a transformation would appear to be statistical, i.e. order–disorder, rather than purely displacive.

Cooper (1967) discussed the situation for α -AlFeSi which has space group $Im\bar{3}$. He proposed that α -AlFeSi contains two types of unit cells (cf. our Tables 1 and 3). The average structure belongs to the space group $Im\bar{3}$. Legresy *et al.* (1986) reported coexistence of $Im\bar{3}$ and $Pm\bar{3}$ structures in a specimen of α -AlFeSi. However, we are the first to report the observation of space group $Im\bar{3}$ for α -AlMnSi and the phase transformation for thin specimens. The $Im\bar{3}$ to $Pm\bar{3}$ transition mechanism would appear to involve some rearrangement of the Al(3, 3a), Al(6, 6a) and Al(7, 7a) sites for the third and fourth polyhedral shells (refer to the structural parameters in Tables 2 and 3).

7. Conclusion

The agreement obtained between experimental and calculated HRTEM images is actually quite remarkable for such a complex alloy phase, imaged at 1.7 Å. Such an exhaustive electron optical analysis of a complex alloy phase has not been attempted previously using these techniques. The structure was examined for six distinct zone axes; including both the normal crystallographic and the non-crystallographic zone axes of structural motifs related to $m\bar{3}5$ icosahedral symmetry. The $Im\bar{3}$ structural model proposed by Cooper (1967) for α -AlFeSi has been applied successfully to the case of α -AlMnSi, at least for thin edges of the specimens as observed here by HRTEM.

The significance of the present work, both the experiments and the image simulations, is that they provided us with a realistic understanding of the limitations of HRTEM techniques for imaging the quasicrystalline alloy α -AlMnSi. Thus we are confident that the requirements for obtaining so-called structure images of complex alloy structures may be met experimentally and that the images may be reliably interpreted on the basis of computer simulation and image-matching at about 0.17 nm resolution. However, it is disappointing to report that there seems little prospect of being able to distinguish between DMI and MI using HRTEM at this resolution, although the positions of the icosahedral clusters may be located for [100] axis images.

We note that most difficulty was experienced in obtaining the experimental images, especially so for the non-crystallographic zones, which were very sensitive to slight changes in orientation of the specimen, to the wedge angle and to the orientation of the top and bottom surfaces of the specimen. All of these effects modify the shape transform of the thin specimen and its interaction with the Ewald sphere. Other problems concern location of sufficiently thin areas of specimen and the avoidance of undue electron beam induced specimen contamination or transformation to amorphous material. Great care with specimen preparation was also necessary as the thinned alloy specimens tend to develop an amorphous surface layer on exposure to air, which tends to degrade the HRTEM image of the crystalline phase.

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References

- Barry, J. C., Bursill, L. A., and Sanders, J. V. (1985). *Aust. J. Phys.* **38**, 437–48.
- Bergman, G., Waugh, J. L. T., and Pauling, L. (1952). *Nature* **169**, 1057–8.
- Bursill, L. A., and Peng, J. L. (1985). *Nature* **316**, 50–1.
- Bursill, L. A., Peng, J. L., and Fan, X. D. (1992). *Aust. J. Chem.* **45**, 1527–46.
- Cooper, M., and Robinson, K. (1966). *Acta Crystallogr.* **20**, 614–17.
- Cooper, M. (1967). *Acta Crystallogr.* **23**, 1106–7.
- Fowler, H. A., Mozer, B., and Sims, J. (1988). *Phys. Rev. B* **37**, 3906–13.
- Goldman, A. I., and Kelton, R. F. (1993). *Rev. Mod. Phys.* **65**, 213–30.
- Goodman, P., and Moodie, A. F. (1974). *Acta Crystallogr. A* **30**, 280–90.
- Hiraga, K., and Shindo, D. (1990). *Mater. Trans. Japan. Instit. Metal* **31**, 567–72.
- Legresy, J. M., Audier, M., Simon, J. P., and Guyot, P. (1986). *Acta Metallurg.* **34**, 1759–69.
- Pauling, L. (1985). *Nature* **317**, 512–14.
- Peng, J. L., and Bursill, L. A. (1990). ‘Quasicrystals, Networks and Molecules of Fivefold Symmetry’ (Ed. I. Hargittai), Ch. 4, pp. 49–67 (VCH Publishers: New York).
- Song, G. L. (1997). PhD Thesis, University of Melbourne.
- Song, G. L., and Bursill, L. A. (1997a). Electron diffraction study of α -AlMnSi alloys including non-crystallographic zone axes, in press.
- Song, G. L., and Bursill, L. A. (1997b). Computer simulation of HRTEM images of quasicrystalline α -AlMnSi alloys, in press.
- Tibballs, J. E. (1990). *Key Engin. Mater.* **44/45**, 233–46.
- Tibballs, J. E., Davis, R. L., and Parker, B. A. (1989). *J. Mater. Sci.* **24**, 2177–82.
- Yang, Q. B. (1988). *Philos. Mag. B* **61**, 155–75.

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