STRUCTURE OF THE "ICOSAHEDRAL" PHASE IN RAPIDLY SOLIDIFIED ALUMINIUM-MANGANESE ALLOYS

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ABSTRACT

The different types of non-equilibrium phases produced by rapid solidification of metallic melts are reviewed. The recent developments following the detection of crystallographically forbidden five-fold symmetry in electron diffraction patterns of rapidly solidified Al-14% Mn alloy are chronicled briefly, listing the efforts thus far to explain experimental observations either within or outside the framework of classical crystallography.

After reviewing some special features and types of imperfections associated with rapidly solidified crystalline phases, the available diffraction data on the Al-Mn "icosahedral" phase are examined from the standpoint of traditional crystallography. It is shown that the d_{hkl} values of all X-ray, neutron and electron reflections from this new phase are satisfactorily accounted for on the basis of traditional, but complex tetragonal crystal structure with unit cell dimensions of $a = b = 16.528$ Å and $c = 17.356$ Å. The possible atomic arrangements and likely structural irregularities in this intermetallic phase are discussed, keeping in view its chemical composition, physical properties and mechanical behaviour.

INTRODUCTION

THE different types of non-equilibrium phases produced by rapid solidification of alloys have fascinated metallurgists and materials scientists alike for well over a quarter of a century now. As early as in 1952 Falkenhagen and Hoffmann[1] demonstrated the possibility of producing non-equilibrium, supersaturated solid solutions in alloys based on aluminium, including Al-Mn alloys, by increasing the cooling rate during solidification of the alloy melts. However, the era of rapidly solidified alloys is generally accepted to have begun in 1960 with the spectacular series of elegant experiments performed by Duwez and his co-workers[2,3] with their now-famous "gun" technique capable of generating very high cooling rates, even exceeding 10^6 K/s. In the space of one year, Duwez *et al* achieved isomorphous solidification or unlimited extension of solid solubility in the Cu-Ag system, established formation of new crystalline phases in the Ag-Ge and Au-Ge systems and produced the first-ever metallic glass in eutectic Au-Si alloy. The sixties and seventies brought forth a rich harvest[4] of over 2000 publications on non-equilibrium solid solutions, crystalline phases and metallic glasses produced by several rapid solidification techniques in diverse binary, ternary and even more complex alloy systems. The eighties have now witnessed wide commercial exploitation of the technological potential of rapid solidification processing of metallic melts.

The amazing story of academic curiosity and milligram-capacity laboratory devices paving the way for a new high-speed casting technology and its successful engineering to produce thousands of tons of different new-generation alloys has been told many times in recent years. It has just been unfolded comprehensively in a new book[5], with all its gripping details and global ramifications.

A new development was heralded in the field of rapid solidification when Sastry *et al*[6] reported in 1978 on the rather surprising display of "pseudo-pentagonal" symmetry by a rapidly quenched Al-6% Pd alloy in its electron diffraction patterns. This revelation of crystallographically forbidden five-fold symmetry baffled these workers who concluded that they were dealing with a highly defective structure displaying many interesting crystallographic phenomena like stacking faults, periodic twinning, anti-phase domains, etc. This intriguing observation did not attract much attention until Shechtman *et al*[7] published in 1984, similar, but more explicit electron diffraction patterns from a new phase in rapidly solidified Al-14% Mn alloys and explained them on the basis of icosahedral point group symmetry $m\bar{3}5$,

which is inconsistent with translational periodicity. In view of the observed quasi-periodicity in this exotic phase, Levine and Steinhardt[8] suggested the name "quasicrystals" for this and other similar "icosahedral" phases. Starting from early 1985 the possibility of a new type of atomic order in solids and consequently the possible existence of a new species of solid materials with unusual properties have fired the imagination of different groups of scientists from all over the world and unleashed an almost feverish research activity to produce, study and understand "icosahedral" phases similar to those first discovered in Al–Pd and Al–Mn alloys. Over 600 papers have appeared already in this area of research.

It is a measure of the intense involvement of scientists of different disciplines in these new intermetallic phases that two International Workshops have already been held on these phases viz. the first[9] on "Aperiodic crystals" at Les Houches, France, in March 1986 and the second[10] on "Quasicrystals" at Beijing, China, in September 1987 and their proceedings published in record time. Just a year ago *Scripta Metallurgica* published[11] a set of papers on these phases.

Following the discovery of the new Al-Mn phase, Ramachandrarao and Sastry[12], and Zhang *et al*[13] postulated that equilibrium alloy phases having icosahedral clusters of atoms in their unit cells might well give rise to "icosahedral" phases on rapid solidification and actually synthesized these unusual phases on this basis in Al-Zn-Mg and Ti-Ni-V alloys respectively. Such phases have since been reported[14–18] in Al-(Mn, Cr, Fe, V, W, --) binary systems, Al-Si-Mn, Al-Zn-Mg, Al-Cu-Mg, Al-Li-Cu, Ti-V-Ni, Al-Si-Cr, Ga-Zn-Mg, Pd-Si-U ternary systems and many quaternary systems based on the latter. A majority of these phases form in composition ranges where the equilibrium phases are of the Frank-Kasper type (cubic with 162 atoms in the unit cell), in which icosahedral coordination shells dominate the structure[19].

Since the discovery of the unusual Al-Mn phase, a new type of "quasicrystal" has been reported[20–23] in Al-Mn, Al-Co and Al-Fe alloys. Referred to as the decagonal phase, this has a ten-fold axis with the structure normally periodic *along* the axis, but similar to the "icosahedral" phase in the directions *perpendicular* to it.

Understandably, many approaches have been made to explain the atomic arrangements in these exotic phases on the basis of models, most of them assuming quasicrystallinity and a few within the broad framework of traditional crystallography. These models are generally concerned with explaining observed diffraction effects and can be broadly classified under the following three heads: (i) Three-dimensional penrose tiling (3-DPT)[8,24–26]; (ii) Dense packing of icosahedra (DPI)[27–29], and (iii) Complex crystals with twins (CCT)[30–32].

Needless to say, any model for the structure of these new phases should aim at accounting ideally for all — and in practice most — experimental observations related to these phases, thus explaining not only the diffraction effects but also microstructural features, chemical compositions, physical, chemical and mechanical properties and responses to thermal, deformation, chemical and irradiation treatments. So far, however, none of the models has been able to explain even all the observed diffraction effects viz. peak positions, peak intensities and peak broadening.

In this paper an attempt is made to analyse all available X-ray, neutron and electron diffraction data for the new Al-Mn phase from the standpoint of traditional crystallography and to establish the unit cell, if at all it exists for this "icosahedral" phase. The possible role of known crystalline imperfections like twinning, faulting, strains, etc. in the appearance of unusual diffraction effects and microscopic features associated with this phase are also examined.

RELEVANT STRUCTURAL DATA

Before considering the nature of the new "icosahedral" phases, it is instructive — in fact, quite necessary — to review what is already known about non-equilibrium and equilibrium metallic phases based on face centred cubic (fcc) metals, particularly aluminium.

Disorder and imperfections seem to abound in many rapidly solidified alloys. This fact should not be surprising in view of the rather abnormal conditions and fast rates of growth of solid phases during rapid solidification. At one end we have the metallic glasses[33], whose diffraction effects suggest atomic arrangements in them very similar to those in the concerned melts. Starting with the well known Bernal model of dense random packing of hard spheres, originally developed for monoatomic liquids, many models have been developed to explain the diffraction data from both metal-metalloid and metal-metal glasses. While *qualitative* agreement has been claimed for most models, *quantitative* agreement has not been forthcoming for

any model, despite the ready assistance of sophisticated computers to refine and modify the most complex models to the full satisfaction of the model makers!

It is relevant, in the context of the observed "icosahedral" symmetry in Al-Mn and many other intermetallic phases, to note that *local* icosahedral order was suggested by Frank[34] as early as in 1952 as an explanation for the undercooling of liquid metals. The concepts of pentagonal chains formed by linking the Frank icosahedra of 13 atoms each was later put forward by Hume-Rothery and Anderson[35] to explain the unusual compositions of eutectics in binary alloy systems. The close inter-relationship between liquid, quasi-crystalline, glassy and even crystalline phases like the Frank-Kasper ones in some alloy systems and the promise of a unified model for icosahedral order in glasses, quasi-crystalline and crystalline materials have since been highlighted[36,37]. It is also interesting to note here how the 13-atom icosahedral unit seems to figure in some way in many crystalline phases[38] like $Al_{12}W$, $Al_{12}Mo$, $Al_{12}Mn$, $Al_{12}Cr$, etc. (body-centred cubic, 26 atoms in the unit cell)[39] $Al_5Mg_2Cu_6$ (cubic, 39 atoms in the unit cell)[40] and Al_8Mn_5, Al_8Cr_5, etc. (rhombohedrally distorted bcc, 52 atoms in the unit cell)[41].

As regards metastable crystalline phases produced by rapid quenching of metallic melts, considerable work of relevance to the present theme has been done by the present author and his co-workers[42–52] on alloys based on fcc metals like aluminium, silver and gold. There have been reports on non-equilibrium hexagonal close packed (hcp) phases[43], often characterized by varying densities of random stacking faults[50], that contribute to anomalous X-ray diffraction broadening[46] and to streaking as well as continuous intensity distribution in electron diffraction patterns[47] in a direction perpendicular to the close-packed planes. Many unusual and complex crystalline phases, *occasionally with* very large unit cells, have been detected[44,45,48–52]. Strong preferred orientation, diffraction broadening as well as peak shifts due to different structural irregularities, small coherently diffracting domains, overlapping reflections from phases with large unit cells and twinning on different scales have all been observed in rapidly solidified alloys. In case of phases displaying a few strong and many weak X-ray reflections, the suggestion has been made[42,43] that superlattices or ordered phases based on supersaturated fcc solid solutions could well be the explanation for the experimental observations.

The equilibrium phases in aluminium-transition metal systems are also known for their complexity and special features[53]. They generally feature prominent layers of atoms of transition metals, the transition elements generally avoiding each other. There is a zone of strong reflections corresponding to interplanar spacing of about 2 Å, around the Al_{111} and Al_{200} reflections. The ten-fold coordination group of aluminium atoms has a distinctive shape related to the icosahedron, with the vertices removed.

The aluminium-manganese system itself is known[54] for its many equilibrium intermediate phases, although there is uncertainty regarding some of the crystal structures and modes of their formation[55]. Starting from the aluminium side, the following phases have been reported:

1. $Al_{12}Mn$ bcc $a = 7.507$ Å
2. Al_6Mn Orthorhombic $a = 6.498$ Å; $b = 7.512$ Å and $c = 8.870$ Å
3. Al_4Mn Hexagonal $a = 28.35$ Å; $c = 12.36$ Å
4. $Al_{10}Mn_3$ Hexagonal $a = 7.54$ Å; $c = 7.90$ Å
5. Al_3Mn Orthorhombic $a = 14.79$ Å; $b = 12.42$ Å; $c = 12.59$ Å
6. Al_8Mn_5 Rhombohedral $a = 9.06$ Å; $\alpha = 89.3°$
7. AlMn Hexagonal $a = 19.95$ Å; $c = 24.52$ Å.

There seem to be a geometric relationship between some of them and a few can perhaps be assigned related crystal structures.

UNIT CELL OF THE NEW PHASE

In the light of the foregoing, all available X-ray, neutron and electron diffraction data for the Al-Mn "icosahedral" phase[56,57] were examined to find out whether they can be satisfactorily explained on the basis of a *single* unit cell on traditional crystallographic lines. In this connection, it was noted that Pauling[31] had proposed complex cubic unit cells, first with $a = 26.73$ Å and then with $a = 23.36$ Å, for this phase, but without trying to explain *all* observed interplanar distances (d_{hkl} values) on the basis of either. Strong reflections were indexed, but some *hkl* values were rather unusual and unconvincing. Although his proposal for twinning had the support of a few other investigators[30,32], the whole argument in favour of a normal crystal structure for this phase, but with unusual imprefections, suffered for want of a unit cell that can explain all observed X-ray, neutron and electron reflections. Hence it invited criticisms which are now well-documented[58–60].

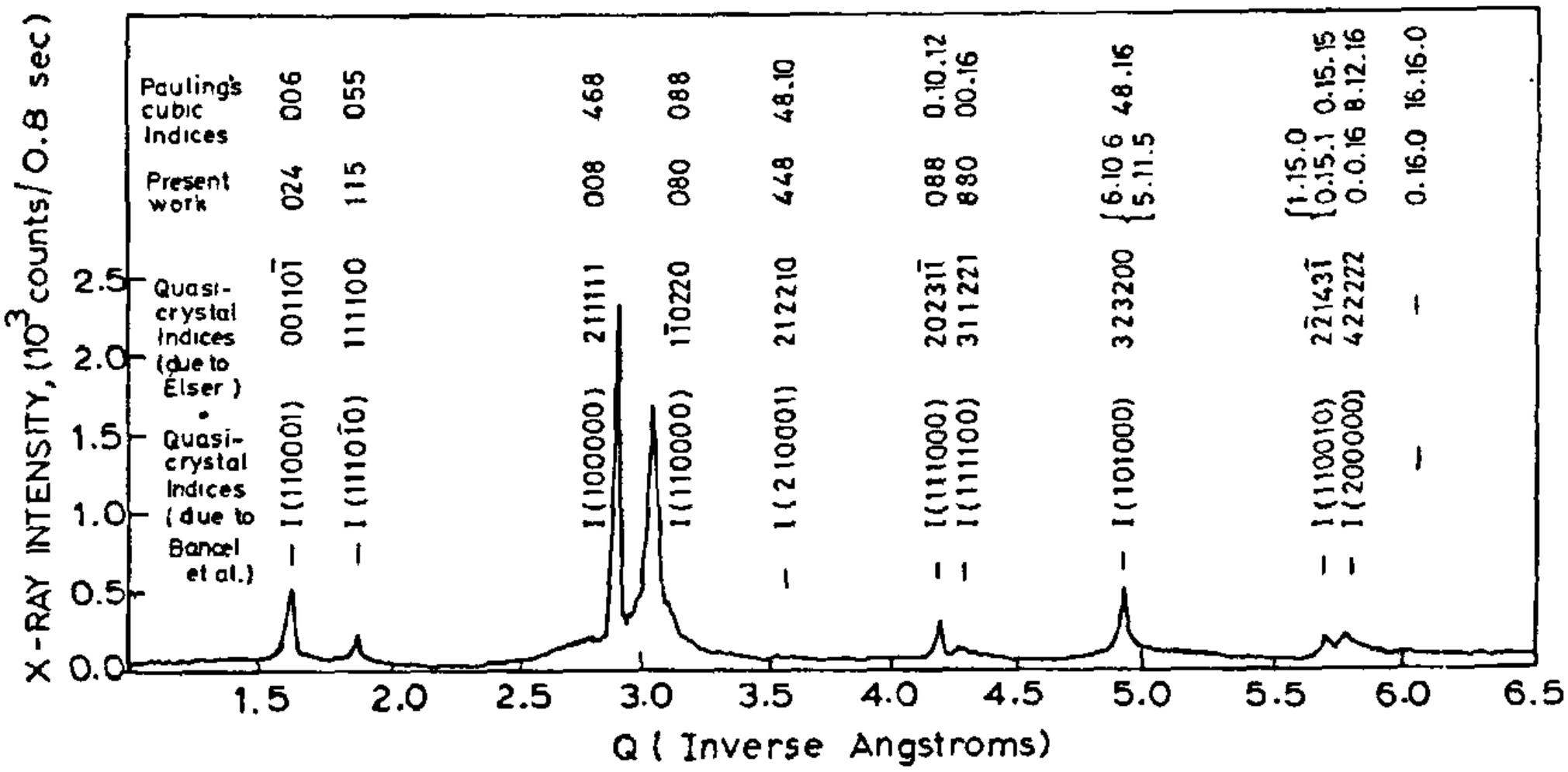

Figure 1. X-ray diffraction profile from the new Al-Mn phase with different indices on the basis of two quasicrystalline models and two crystalline unit cells (profile based on reference 56).

The case for complex twinning in a traditional, but rather special crystalline phase has been stated quite emphatically by Carr[32] and the diverse twinning possibilities have recently been analysed by Wadhawan[61]. The complexities of twinning in derivatives of bcc and fcc lattices have also been recently highlighted[62]. Diffraction broadening and peak shifts from crystalline phases containing random twins or growth faults on close-packed atomic planes have already been referred to in the previous sections.

Thus the search for a suitable unit cell for the new Al-Mn phase was conducted, keeping in view its likely capacity to twin in unusual ways and also to develop growth stacking faults. The results of this analysis are brought out in figure 1, and tables 1 and 2. All observed reflections are indexed satisfactorily on the basis of a large tetragonal unit cell with $a = b = 16.528$ Å, $c = 17.356$ Å and $c/a = 1.050$. The agreement between observation and calculation is quite good, considering the uncertainties in the locations of weak and broad peaks, particularly at low Bragg angles. Understandably the fitting of observed and calculated d_{hkl} values becomes easier for reflections with higher Bragg angles, overlapping of two or more reflections becoming a rule rather than an exception and making its own contribution to diffraction broadening of the concerned peaks.

One of the criticisms against the Pauling proposal has been[63] that it seems almost impossible to introduce so many extinction rules to eliminate all unwanted peaks from the diffraction pattern. Apart

Table 1 *Observed and calculated interplanar spacings (Å) and observed relative intensities for X-ray, neutron and electron reflections from the icosahedral Al-Mn phase (Tetragonal unit cell: $a = b = 16.528$ Å and $c = 17.356$ Å; Reflections observed by all three techniques are underlined)*

Observed d_{hkl} values			Observed intensities			Calculated			
X-ray	Neutron	Electron	X-ray	Neutron	Electron	d_{hkl}	h	k	l
1	2	3	4	5	6	7	8	9	10
9.520	–	–	<1	–	–	9.694	1	1	1
–	–	8.300	–	–	vw	8.264	0	2	0
5.416	–	5.400	<1	–	w	5.460	0	1	3
						5.252	0	3	1
3.850	3.855	3.859	22	202	w	3.878	1	3	3
						3.842	0	2	4
3.349	3.335	3.320	8	114	w	3.338	1	3	4
						3.328	1	1	5
						3.295	1	4	3
3.142	–	–	<1	–	–	3.186	1	5	1
						3.142	1	2	5
2.856	–	–	2	–	–	2.870	0	5	3
						2.835	3	5	0
						2.828	1	5	3
–	2.622	–	–	38	–	2.626	0	6	2
						2.613	2	6	0
2.523	2.527	–	3	163	–	2.545	3	5	3
2.379	–	–	<1	–	–	2.394	3	4	5
						2.373	3	5	4

(*contd...*)

1	2	3	4	5	6	7	8	9	10
(table 1 contd...)									
						2.370	0	4	6
						2.369	1	5	5
2.336*	–	–	?	–	–	2.340	0	7	1
						2.337	1	7	0
						2.326	0	6	4
						2.322	3	3	6
						2.317	5	5	1
2 170	2.172	2 167	100	100	vs	2.170	0	0	8
						2.167	5	5	3
2 065	2 068	2 066	78	69	vs	2.066	0	8	0
						2.058	1	7	4
						2 056	4	4	6
2.027	–	–	<1	–	–	2 036	4	7	1
						2.034	2	2	8
						2.027	4	6	4
1.939	–	–	<1	–	–	1 948	6	6	0
						1.939	2	6	6
						1.939	1	7	5
						1 932	1	8	3
–	1.912	–	–	24	–	1.921	0	4	8
						1.921	5	7	0
						1.910	5	7	1
						1.903	1	1	9
1.826	–	–	<1	–	–	1.840	3	7	5
						1.823	5	7	3
–	1.817	–	–	55	–	1.818	5	5	6
						1.815	1	9	1
						1.809	1	3	9
						1.807	4	8	2
1.757	1.755	–	2	54	–	1.765	4	7	5
						1.757	5	7	4
						1.748	3	6	7
						1.742	4	4	8
1.731	–	–	<1	–	–	1.736	3	7	6
						1.733	3	9	1
						1.728	3	3	9
						1.723	3	5	8
–	–	1.662	–	–	vvw	1.666	3	4	9
						1.664	2	2.10	
						1.662	7	7	1
						1.657	1	5	9
1.603	1.599	–	1	33	–	1 600	1	4.10	
						1.599	5	9	1
1 496	1.493	1.497	11	52	vvw	1.497	0.11.	1	
						1.496	1.11.	0	
						1.496	0	8	8
						1.494	0	7	9
						1.492	4	4.10	
1.459	1.455	–	3	12	–	1.462	3.	3	11
						1.461	8	8	0

(contd...)

1	2	3	4	5	6	7	8	9	10
(table 1 contd...)									
						1.457	5	9	5
						1.453	6	7	7
1.428	–	–	1	–	–	1.432	2.11.	3	
						1.430	3.11.	2	
						1.425	3	9	7
1.366	1.364	–	–	106	–	1.368	5.11.	0	
						1.366	3	8	9
						1.365	0	4.12	
						1.364	5.11.	1	
1.337	–	–	1	–	–	1.342	2.12.	2	
						1.338	7	9	5
						1.338	3.11.	5	
						1.336	1.12.	3	
						1.334	3 10.	7	
1.275	1.274	1.277	20	54	s	1.281	0.	6.12	
						1.281	1.11.	7	
						1.277	8 10.	2	
						1.276	3	7.11	
						1.273	5.11.	5	
						1.273	6.10.	6	
						1.270	2.11.	7	
1.259	1.259	–	1	10	–	1.263	3	3.13	
						1.258	1	9	10
						1.254	1.13.	2	
						1.254	7.11.	2	
						1.253	2.13.	1	
1.213	–	–	1	–	–	1.213	2	2.14	
						1.212	8	8	8
						1.212	8.11.	1	
						1.211	3.13.	3	
1.201	–	–	1	–	–	1.203	7	7.10	
						1.201	8	9	7
						1.201	1.12.	7	
						1.198	16.13		
						1.198	6	9	9
1.141	–	–	1	–	–	1.141	44.14		
						1.140	9.11.	3	
						1.139	4	8.12	
1.101	–	–	5	–	–	1.100	0.15.	1	
						1.099	1.15.	0	
						1.099	3	8.13	
						1.098	6.10.10		
1.085	–	–	7	–	–	1.086	1.11.11		
						1.085	0	0 16	
						1.085	6.14.	0	
						1 084	10.10.	6	
1.078	–	–	3	–	–	1.080	1.15.	3	
						1.079	2.10.12		
						1.079	2.11.11		
						1.077	9	9	9

(contd ..)

1	2	3	4	5	6	7	8	9	10
(*table 1 contd...*)									
						1.077	6.	14.	2
						1.037	1	10.	13
1.037	–	1.033	1	–	w	1.037	55.	15	
						1.037	17.	15	
						1.037	0.	14.	8
						1.036	8.	10.	10
						1.036	1.	12.	11
						1.036	9.	10.	9
						1.034	5.	11.	11
						1.033	9.	16.	0

* Possible overlap of aluminium reflection:
$d\,Al_{111} = 2.338$ Å.

$d\,Al_{022} = 2.024$ Å; $d\,Al_{113} = 1.221$ Å.

from the fact that many very weak reflections have perhaps not been recorded in practice, the data in table 1 emphatically bring out the fact that we are here concerned with a slightly tetragonally distorted and large *cubic* unit cell, possibly with some ordering of the Al and Mn atoms. The indices follow the fcc pattern viz. h, k and l are *all* odd or *all* even, except that reflections with $(h + k + l)$ divisible by *four* are *also* present. Reflections with h, k and l *all* even common for fcc and bcc structures seem to be the strong ones. As mentioned earlier, some expected reflections are missing, but then no special efforts seem to have been made in the X-ray and neutron studies thus far to locate the very weak reflections. It is also relevant to point out here that the strong reflections (figure 1) from this phase have indices whose values inspire more confidence in the proposed crystal structure than was the case with Pauling's cubic unit cells[31] with much larger volumes.

Table 2 *Indices and interplanar spacings of the new Al-Mn phase highlighting its structural relationships with Al and* $Al_5Mg_2Cu_6$

Aluminium f.c.c. $a = 4.0494$ Å		$Al_5Mg_2Cu_6$ cubic $a = 8.311$ Å		New Al-Mn phase tetragonal $a = 16.528$ Å, $c = 7.356$ Å		
$h\,k\,l$	d_{cal} (Å)	$h\,k\,l$	d_{cal} (Å)	$h\;k\;l$	d_{cal} (Å)	d_{obs} (Å)
0 0 2	2.025	0 0 4	2.078	0 0 8	2.170	2.170
				0 8 0	2.066	2.065
0 2 2	1.431	0 4 4	1.469	0 8 8	1.496	1.496
				8 8 0	1.461	1.459
2 2 2	1.169	4 4 4	1.197	8 8 8	1.212	1.213
0 0 4	1.012	0 0 8	1.039	0 0 16	1.085	1.085
				0.16. 0	1.033	1.037
0 2 4	0.906	0 4 8	0.929	0 8 16	0.960	0.962
				0.16. 8	0.924	0.924

Table 2 highlights what looks like simple, but special relationships between the fcc unit cell of aluminium (or the solid solution of Mn in Al i.e. α-Al phase) and the cubic unit cell[40] of $Al_5Mg_2Cu_6$ on the one hand and the large tetragonal unit cell of the new Al-Mn phase on the other. The latter may be considered to be made up of either 4^3 i.e. 64 unit cells of α-Al, but with slight lattice expansion, tetragonal distortion and perhaps ordering of the two concerned species of atoms or 2^3 i.e. 8 unit cells of $Al_5Mg_2Cu_6$, but with slight tetragonal distortion due perhaps to ordering. These *structural* relationships need not necessarily imply any *crystallographic* relationships between these phases.

Starting from an fcc unit cell, it is fairly easy to move over to tetragonal, orthorhombic or rhombohedral unit cells by introducing appropriate distortions. As has been shown by Yang[64] in discussing the pentagonal bipyramids of pure gold obtained by vapour deposition, the fcc, bcc and rhom. structures are all closely related *geometrically*.

TOWARDS POSSIBLE ATOMIC ARRANGEMENTS

Following the establishment of the above-referred tetragonal unit cell and its possible structural relationships with α-Al and $Al_5Mg_2Cu_6$ phases, one may now proceed further to consider the possible atomic arrangements in it and also to explain all observations related to the new Al-Mn phase. However, there is a long way to go, since we are obviously dealing with a crystallographically complex as well as faulted material, whose electron micrographs are invariably "dirty", described as mottled, coral-like, facetted, spherulitic, speckly and feathery, in fact as anything but bright and smooth. Evidence for planar faults in such "icosahedral" phases is now available in electron micrographs[65,66], although their appearance as parallel bands is *not* essential[32] for the type of twinning and faulting envisaged in this context. Much has been made from the beginning of the fact that dark-field imaging from any of the ten electron diffraction spots bringing out the icosahedral symmetry lights up the *entire* grain. Actually the ten spots are generally *not* identical in shape and

intensity and the entire grain is never *uniformly* and *identically* illuminated from each imaging, these variations suggesting presence of *several* twin or orientation variants through the foil thickness.

The study of single crystals should normally throw some light on the atomic arrangements but recent Laue and precession photographs of 300 μm-size crystals of Al-Cu-Li "icosahedral" phase[67] have only highlighted some unusual features viz. anisotropic peak shapes with many components in them, non-uniform streaking in different directions, diffuse rings and considerable deviation between observed intensities and those calculated for quasicrystalline models.

The mechanical behaviour of the new Al-Mn and other "icosahedral" phases in displaying brittleness and hardness can perhaps be understood in terms of heavy twinning or faulting and also ordering of the different species of atoms in the unit cell.

The chemical composition of the new Al-Mn has been given[56] in the range of 20–22 at% Mn with a possible chemical formula Al_4Mn, although there are some uncertainties[68] about this stoichiometry. Taking a cue from the already referred 39-atom unit cell of $Al_6Mg_2Cu_6$ phase, one may well assign the formula $Al_{31}Mn_8$ for this phase, in which case the manganese content of the phase will be 20.5 at%, well within the actual range established by experiment. On the basis of this formula the density of the phase works out to 3.58 g.ml^{-1}, again well within the range of estimates available in literature.

Reverting back to the pentagonal chains made up of Frank icosahedral units[35], it is interesting that in liquid alloys richer in manganese the Al and Mn atoms can form only *two* types of chains with Mn atoms either at the *centres* or the pentagon *corners* of the icosahedra, while avoiding Mn-Mn contacts viz.

(1) [1Mn-5Al-1Mn-5Al-1Mn..] with Mn concentration 1/6 or 16.7%.

(2) [1Al-3Al -1Al-4Al -1Al-3Al -1Al-4Al -1Al..]
2Mn 1Mn 2Mn 1Mn
with Mn concentration 1/4 or 25%.

An *equal* distribution of the two chains may be expected to lead to around 20.8 at% Mn in the melt before solidification and also two *distinct* Mn sites in the icosahedral phase after solidification with minor adjustments of atomic positions, even as the crystal growth takes place in ten different directions, as dictated by the symmetry of the pentagonal chains, with many orientation variants and interface distortion between them. This simple picture may have to be refined further, but it explains the observed chemical composition, the equiaxed grains, the propensity to grow penta-twins or five different orientations of the same structure, chemical inhomogenity on nanometer scale[68] and the two different Mn sites brought out by EXAFS studies[69]. The planar faults, small grain sizes, microstructural appearance, shapes of grains, etc. can also be understood on the basis of these models for the melt and the solidification process.

In conclusion, the present work has established the unit cell of the new Al-Mn phase and explained many observations related to its nucleation and growth, as also the somewhat unusual structural features displaced by it. All this has been achieved within the framework of traditional crystallography. However, further work will be necessary to throw more light on a few remaining points like the structure factor of the phase, the nature of the imperfections in it and the diverse electron diffraction patterns obtained from it.

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1. Falkenhagen, G. and Hoffman, U., *Z. Metallk.*, 1952, **43,** 69.
2. Duwez, P., Willens, R. H. and Klement, Jr. W., *J. Appl. Phys.*, 1960, **31,** 1136.
3. Klement, Jr. W., Willens, R. H. and Duwez, P., *Nature (London)*, 1960, **187,** 869.
4. Suryanarayana, C., *Rapidly quenched metals: A bibliography*, Plenum Press, New York, 1980.
5. Anantharaman, T. R. and Suryanarayana, C., *Rapidly solidified metals: A technological overview*, Trans. Tech. Publications, Aedermannsdorf, Switzerland, 1987.
6. Sastry, G. V. S., Suryanarayana, C., Van Sande, M. and Van Tendeloo, G., *Mat. Res. Bull.*, 1978, **13,** 1065.
7. Shechtman, D., Blech, I., Gratias, D. and Cahn, J. W., *Phys. Rev. Lett.*, 1984, **53,** 1951.
8. Levine, D. and Steinhardt, P. L., *Phys. Rev.*

Lett., 1984, **53**, 2477.
9. Gratias, D. and Michel, L. (eds), *Proceedings of the International Workshop of Aperiodic Crystals, J. Phys.*, C3, Supplement No. 7, Vol. 47, 1986.
10. Kuo, K. H. (ed.), *Proceedings of the International Workshop on Quasicrystals*, Trans. Tech. Publications, Aedermannsdorf, Switzerland, 1987.
11. Shechtman, D., *Scr. Metall.*, 1986, **20**, 1185.
12. Ramachandrarao, P. and Sastry, G. V. S., *Pramana—J. Phys.*, 1985, **25**, L225.
13. Zhang, Z., Ye, H. Q. and Kuo, K. H., *Philos. Mag.*, 1985, **A52**, L49.
14. Sastry, G. V. S., Rao, V. V., Ramachandrarao, P. and Anantharaman, T. R., *Scr. Metall.*, 1986, **20**, 191.
15. Mukhopadhyay, N. K., Subbanna, G. N., Ranganathan, S. and Chattopadhyay, K., *Sci. Metall.*, 1986, **20**, 525.
16. Inoue, A., Kimura, H. M. and Masumoto, T., *J. Mater. Sci.*, 1987, **22**, 1758.
17. Chen, H. S. and Inoue, A., *Scr. Metall.*, 1987, **21**, 527.
18. Yamane, H., Kimura, K., Shibuya, T. and Takeuchi, S., *ISSP Technical Report*, 1987, No. 1848, University of Tokyo, Minato-ku, Tokyo, Japan.
19. Pearson, W. B., *The crystal chemistry and physics of metals and alloys*, Wiley, New York, 1972.
20. Bendersky, L., *Phys. Rev. Lett.*, 1985, **55**, 1461.
21. Chattopadhyay, K., Ranganathan, S., Subbanna, G. N. and Thangaraj, N., *Scr. Metall.*, 1985, **19**, 767.
22. Suryanarayana, C. and Jyothi Menon, *Scr. Metall.*, 1987, **21**, 459.
23. Fung, K. K., Yang, C. Y., Zhou, Y. Q., Zhau, J. G., Zhan, W. S. and Shen, B. G., *Phys. Rev. Lett.*, 1986, **56**, 2060.
24. Elser, V. and Henley, C. L., *Phys. Rev. Lett.*, 1985, **55**, 2883.
25. Duneau, M. and Katz, A., *Phys. Rev. Lett.*, 1985, **54**, 2688.
26. Mackay, A. L., *Physica*, 1982, **A114**, 609.
27. Shechtman, D. and Blech, I. A., *Met. Trans.*, 1985, **A16**, 1005.
28. Stephens, P. W. and Goldman, A. I., *Phys. Rev. Lett.*, 1986, **56**, 1168.
29. Guyot, P. and Audier, M., *Philos. Mag.*, 1985, **B52**, L15.
30. Field, R. D. and Fraser, H. L., *Mater. Sci. Engg.*, 1985, **68**, L17.
31. Pauling, L., *Nature* (*London*), 1985, **317**, 512; *Phys. Rev. Lett.*, 1987, **58**, 365.
32. Carr, M. J., *J. Appl. Phys.*, 1985, **59**, 1063.
33. Anantharaman, T. R. (ed.), *Metallic glasses: Production properties and applications*, Trans. Tech. Publications, Aedermannsdorf, Switzerland, 1984.
34. Frank, F. C., *Proc. R. Soc.*, (*London*), 1952, **A215**, 43.
35. Hume-Rothery, W. and Anderson, E., *Philos. Mag.*, 1960, **5**, 383.
36. Widom, M., *Non-linearity in condensed matter*, (eds) A. R. Bishop *et al.*, Springer, Berlin, 1987, p. 330.
37. Anantharaman, T. R., In: *Quasicrystals*, (ed.) K. H. Kuo (Reference 10 above, 1987), p. 55.
38. Shoemaker, D. P. and Shoemaker, C. B., *Acta Crystallogr.*, 1986, **B42**, 3.
39. Schaefer, R. J., Biancaniello, F. S. and Cahn, J. W., *Scr. Metall.*, 1986, **20**, 1439.
40. Samson, S., *Acta Chem. Scand.*, 1949, **3**, 809.
41. Meissner, H. G. and Schubert, K., *Z. Metallk.*, 1965, **56**, 523.
42. Anantharaman, T. R., Luo, H. L. and Klement, Jr. W., *Trans. TMS-AIME.*, 1965, **233**, 2014.
43. Luo, H. L., Klement, Jr. W. and Anantharaman, T. R., *Trans. Indian Inst. Met.*, 1965, **18**, 214.
44. Anantharaman, T. R., Luo, H. L. and Klement, Jr. W., *Nature* (*London*), 1966, **210**, 1040.
45. Ramachandrarao, P. and Anantharaman, T. R., *Trans. TMS-AIME*, 1969, **245**, 886.
46. Ramachandrarao, P. and Anantharaman, T. R., *Philos. Mag.*, 1969, **20**, 201.
47. Furrer, P., Anantharaman, T. R. and Wardimont, H., *Philos. Mag.*, 1970, **20**, 873.
48. Ramachandrarao, P. and Anantharaman, T. R., *Trans. Indian Inst. Met.*, 1970, **23**, 58.
49. Suryanarayana, C. and Anantharaman, T. R., *J. Mater. Sci.*, 1970, **5**, 992.
50. Ramachandrarao, P., Rama Rao, P. and Anantharaman, T. R., *Z. Metallk.*, 1970, **61**, 471.
51. Suryanarayana, C. and Anantharaman, T. R., *Mater. Sci. Engg.*, 1974, **13**, 73.
52. Anantharaman, T. R., Ramachandrarao, P., Suryanarayana, C., Lele, S. and Chattopadhyay, K., *Trans. Indian Inst. Met.*, 1977, **30**, 423 and 434.
53. Bland, J. A., *Acta Crystallogr.*, 1958, **11**, 236.
54. Shunk, F. A., *Second supplement on metallurgi-*

cal equilibrium diagram, McGraw-Hill, New York, 1969.
55. Bendersky, L., Schaefer, R. J., Biancaniello, F. S., Boettinger, W. J., Kaufman, M. J. and Shechtman, D., *Scr. Metall.*, 1985, **19**, 909.
56. Bancel, P. A., Heiney, P. A., Stephens, P. W., Goldman, A. I. and Horn, P. W., *Phys. Rev. Lett.*, 1985, **54**, 2422.
57. Bellisent, R., Bouree-Vigneron, F. and Sainfort, P., *J. Phys.*, 1986, **47**, C3-361.
58. Cahn, J. W., Gratias, D. and Shechtman, D., *Nature* (*London*), 1986, **319**, 102.
59. Mackay, A. L., *Nature* (*London*), 1986, **319**, 103.
60. Bancel, P. A., Heiney, P. A., Stephens, P. W. and Goldman, A. L., *Nature* (*London*), 1986, **319**, 104.
61. Wadhawan, V. K., *Phase Transition*, 1987, **9**, 297.
62. Christian, J. W. and Laughlin, D. E., *Scr. Metall.*, 1987, **21**, 1131.
63. Egami, T. and Poon, S. J., *Proceedings of RQ-6*, Montreal, Canada, August, 1987 (in press).
64. Yang, C. Y., *J. Cryst. Growth*, 1979, **47**, 274 and 283.
65. Perez-Ramirez, J. G., Perez, R., Reyes Gasga, J. and Jose-Yacaman, M., *Scr. Metall.*, 1987, **21**, 1219.
66. Venkateswara Rao, V. and Anantharaman, T. R. (to be published).
67. Denoyer, F., Heger, G., Lambert, M., Lang, J. M. and Sainfort, P., *J. Phys.*, 1987, **48**, 1357.
68. Knowles, K. M. and Stobbs, W. M., *Nature* (*London*), 1986, **323**, 313.
69. Sadoc, A., Flank, A. M., Larade, P., Sainfort, P. and Bellissent, R., *J. Phys.*, 1986, **47**, 873.

NEWS

INDO–U. K. COLLABORATIVE RESEARCH IN FIBRE OPTICS

A research collaboration in the field of fibre optics and optical communication systems has been agreed between the Indian Institute of Technology (IIT), Delhi, and the University of Strathclyde and the British Telecom Research Centre. The collaborative research will be funded under the Indo-British technical co-operation programme.

Fibre optics enables the transmission of light from a precisely defined input point, via a flexible link, to a precisely defined output point. The input and output points may be separated by distances ranging from a few metres to over 100 kilometres, and the light may be modulated either at the input to form a communication system, or during the transmission along the fibre to form an environmental sensing, or information processing system.

(For more details please contact: British Information Services, British High Commission, Chanakyapuri, New Delhi 110 021.)

SAVING LIVES BY SAVING PLANTS

Plants have been used as medicine for millennia. They are a major element of health care systems that rely on traditional medicine but also play an important role in Western medicine. Many of these plants are under threat and it is estimated that if present trends continue, by the turn of the century, some 20,000 plants used in traditional medicine as healing agents may have become extinct.

In order to assess the use of medicinal plants in different communities and to give advice to governments on the conservation and utilization of such plants, a major International Consultation on Conservation of Medicinal Plants, organized jointly by the World Health Organization (WHO), the International Union for the Conservation of Nature, and the World Wildlife Fund, Gland, Switzerland, met in Chiang Mai, Thailand, from 21 to 26 March.

In reaffirming their commitment to the collective goal of Health for All by the Year 2000 through a primary health care approach, the participants at the meeting, unanimously adopted an official Declaration of ten points.

(Further particulars may be had from WHO Media Service, 1211, Geneva 27, Switzerland.)