

## Electron and x-ray diffraction studies on $\text{Al}_{86}\text{Fe}_{14}$ , $\text{Al}_{82}\text{Fe}_{18}$ and $\text{Al}_{75}\text{Fe}_{25}$ quasicrystals

J A SEKHAR, T RAJASEKHARAN, P RAMA RAO,  
G PARTHASARATHY\*, S RAMKUMAR\*\*, E S R GOPAL\*\*†,  
C S LAKSHMI\*\*\* and R M MALLYA\*\*\*

Defence Metallurgical Research Laboratory, Hyderabad 500258, India

\*Instrumentation and Services Unit, \*\*Department of Physics, \*\*\*Department of Metallurgy, Indian Institute of Science, Bangalore 560012, India

**Abstract.** Electron and x-ray diffraction experiments on the melt-spun  $\text{Al}_{100-x}\text{Fe}_x$  ( $x = 14, 18, 25$ ) alloys are carried out. It is observed that all the melt-spun alloys possessing the quasi-crystalline phases have icosahedral point-group symmetry.

**Keywords.** Quasicrystals; structural studies; electron diffraction; x-ray diffraction.

**PACS No.** 61.50; 61.55; 64.70

### 1. Introduction

The observation of sharp electron diffraction spots with icosahedral symmetry in a rapidly quenched alloys of aluminium and manganese by Shechtman *et al* (1984) is a significant discovery in condensed matter physics, since, according to the rigorously proven theorems of crystallography, the icosahedral symmetry is disallowed for crystals. Electron microscopic studies have shown that the material contains 1-2  $\mu$ -size grains of quasicrystals having an icosahedral structure, embedded in the remaining crystalline alloy. This interesting subject has become the object of many investigators, reviewed in several places (Mackay and Kramer 1985; Nelson and Halperin 1985; Ramaseshan 1985; Venkataraman 1985). Besides the Al-Mn system, rapidly-quenched samples of Al-Cr, Al-Fe (Shechtman *et al* 1984), Al-Pd, Al-Ru (Bancel *et al* 1985), Al-Zn-Mg (Ramachandra Rao and Sastry 1985), Al-Cu-Mg (Sastry *et al* 1986), Al-Mn-Si, Al-Mn-Fe (Henley 1985), U-Pd-Si (Poon *et al* 1985), Al-Li-Cu-Mg (Ball and Lloyd 1985), Al-Zn-Cu-Mg (Mukhopadhyay *et al* 1986) and other systems appear to show the icosahedral symmetry. The possibility of space filling tiling or tessellation, showing 5-fold symmetry but not having long range periodicity, was first conceived in the two-dimensional case by Penrose (1974) (see also Gardner 1977) and extended to three-dimensional cases by several workers (Mackay 1982). A possible explanation for the observed 5-fold symmetry, within the bounds of crystallography involves multiple

The authors felicitate Prof. D S Kothari on his eightieth birthday and dedicate this paper to him on this occasion.

† To whom all correspondence should be addressed

scattering from twinned microcrystals defined, perhaps by unit cells containing many atoms (Field and Fraser 1984–85; Pauling 1985). However other evidence from high resolution electron micrography (Hiraga *et al* 1985; Bursil and Lin 1985; Portier *et al* 1985; Guyot and Audier 1985; Knowles *et al* 1985), x-ray diffraction (Bancel *et al* 1985), field ion microscopy and Mössbauer spectroscopy does not support this model (Cahn *et al* 1986, Mackay 1986; Bancel *et al* 1986).

## 2. Experimental details

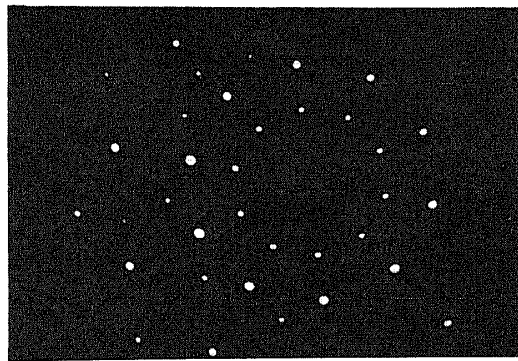
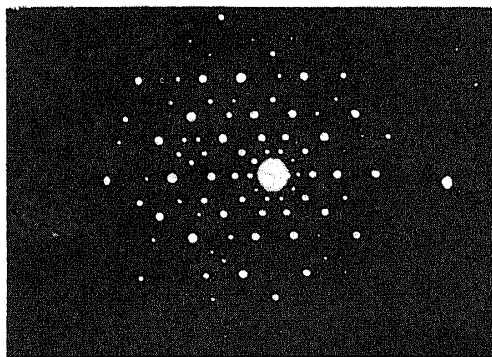
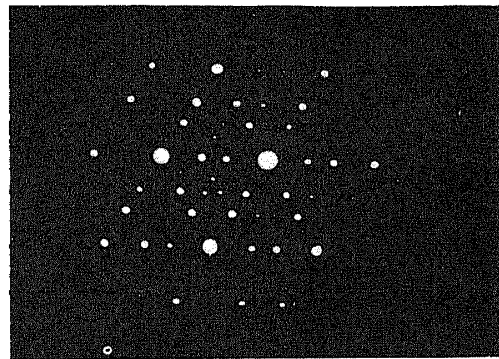
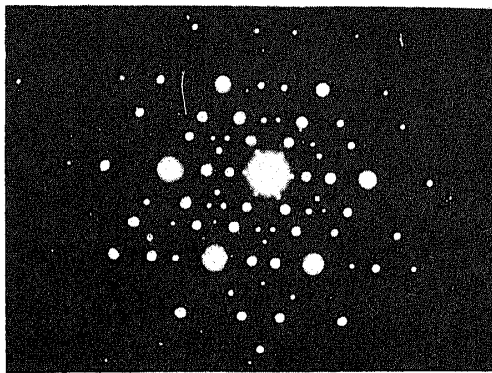
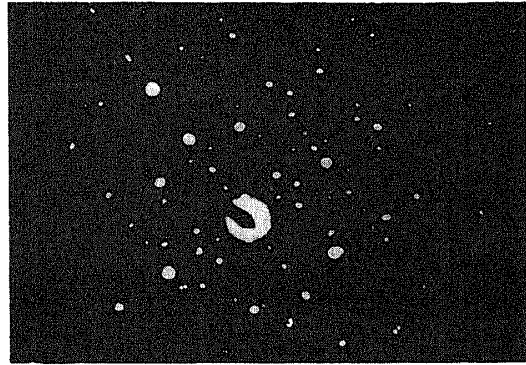
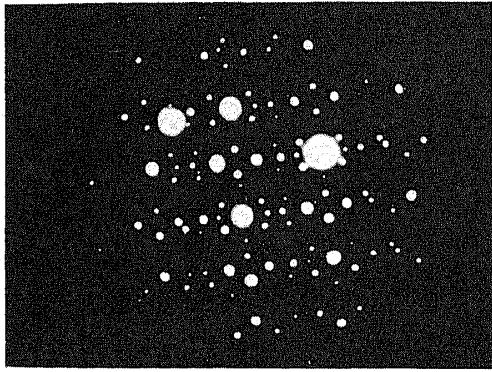
Al-Fe alloys with Fe concentrations of 14, 18 and 25 at. % were prepared by melting, using 99.99% Al and 99.99% Fe. For melt spinning, small pieces cut from the master alloy were induction-heated in quartz tubes. Immediately upon heating, the master alloy was injected onto a copper, melt-spinning wheel, which rotated at 6000 rpm, which produces a cooling rate of the order of  $10^6$  K sec<sup>-1</sup>. The ribbons were typically 2–5 mm wide, 20  $\mu$ m thick, and 10–30 mm in length. Electron diffraction studies were performed in a Philips EM 301 transmission electron microscope. The ribbons were thinned by jet electropolishing in a standard solution of 1.5% HNO<sub>3</sub> and 5% HClO<sub>4</sub> in methanol at a temperature of roughly 250 K. Random sections of the ribbons were tested for the homogeneity of the samples.

## 3. Results and discussion

The selected area electron diffraction patterns of rapidly quenched Al-Fe samples are shown in figures 1, 2 and 3 respectively. Slight tilting and manipulations of the specimens enabled one to locate one of the quasicrystallites and observe the 5-fold symmetric diffraction spots. The icosahedral arrangement was confirmed by observing a three-fold axis at an angle of 37.4° and a 2-fold axis at an angle of 58.3° with respect to the 5-fold axis. The pattern obtained for Al<sub>86</sub>Fe<sub>14</sub>, Al<sub>82</sub>Fe<sub>18</sub> and Al<sub>75</sub>Fe<sub>25</sub> melt spun alloys are shown in figures 1, 2 and 3 respectively. Some of the diffraction patterns obtained from Al<sub>75</sub>Fe<sub>25</sub> samples show other streaks (figure 4) which have been generally interpreted as arising from the *T*-phases (Bendersky 1985; Chattopadhyay *et al* 1985). It appears that the cooling rates are important in deciding the formation and perfection of the quasicrystals. It has been reported that in Al-Mn alloys, if the cooling rate is too high, one obtains a metallic glass with fewer icosahedral grains and if the cooling rate is too low, ordinary crystals of Al-Mn compounds are formed (Heiney 1985; Sekhar 1985). Also it is known that quasicrystalline samples can slowly transform into the crystalline phase. In the case of the Al-Mg-Zn sample this takes place at room temperature within about a week, presumably the crystallization temperature is low (Ramachandra Rao and Sastry 1985).

For the present Al-Fe alloys crystallization temperatures have not been measured, though they are expected to be high. Another cause for the slight differences among the spots could be the differing cooling rates or other conditions of preparations.

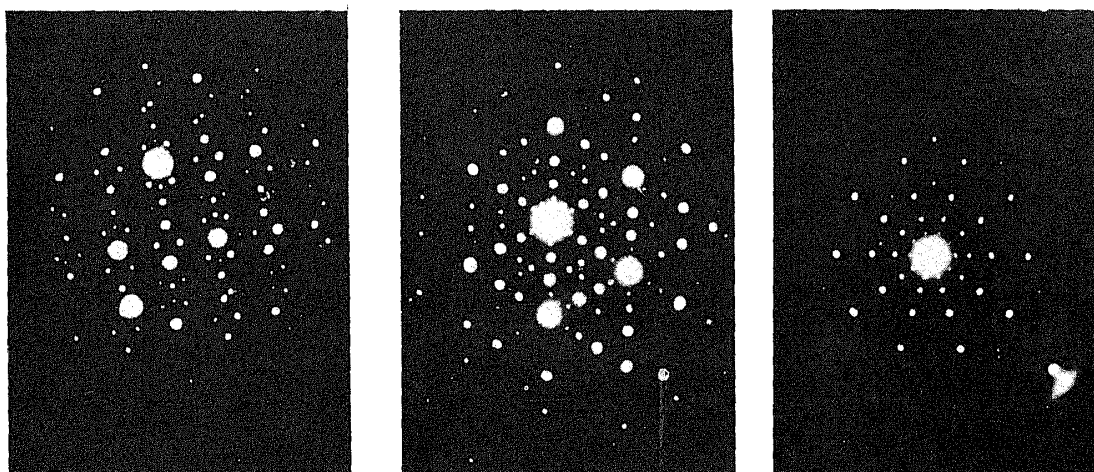
X-ray diffraction data for the specimens were collected, by using a Debye Scherrer camera using the MoK $\alpha$  radiation. They reveal the presence of the quasicrystals embedded in a matrix of aluminium and other materials. In order to index the quasicrystal lines it is convenient to use the 6 index scheme discussed by Elser (1985),



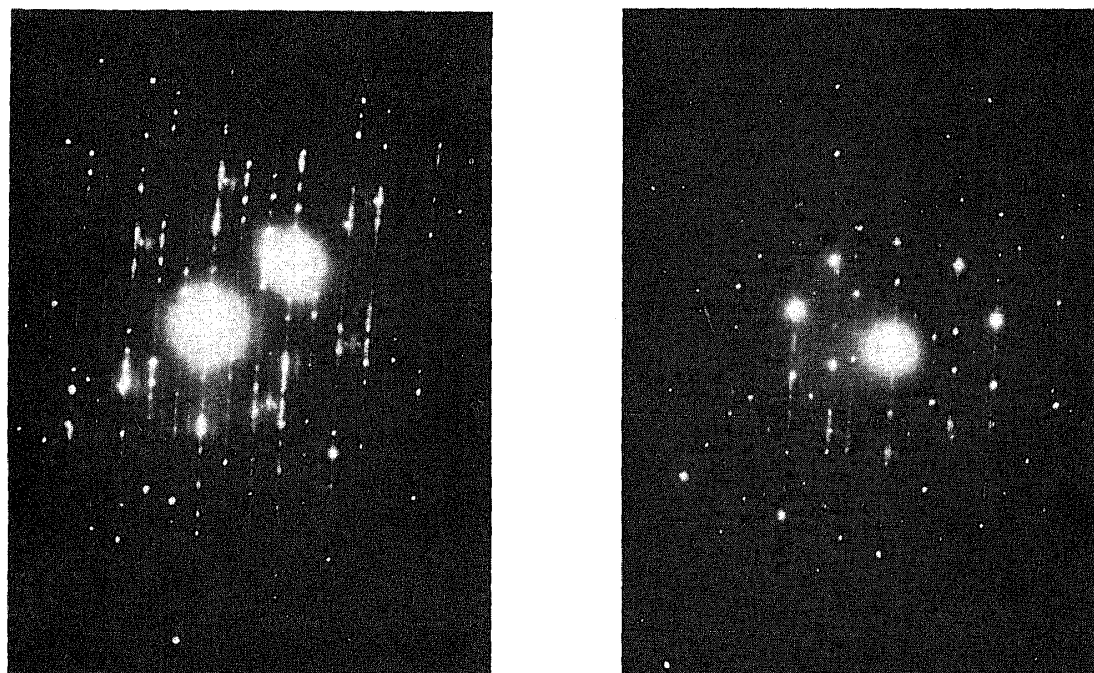
**Figure 1.** Selected area electron-diffraction patterns taken from a single grain in rapidly quenched  $\text{Al}_{86}\text{Fe}_{14}$  alloy. The 5, 3 and 2-fold axes characteristic of  $m\bar{3}5$  (icosahedral) point group symmetry show up clearly. Rotations through  $37.4^\circ$  ( $58.3^\circ$ ) take the 5-fold axis into the 3-fold (2-fold) axis.

**Figure 2.** Selected area electron diffraction patterns taken from a single grain in rapidly quenched  $\text{Al}_{82}\text{Fe}_{18}$  alloy. The icosahedral point group symmetry show up clearly.

Bancel *et al* (1985) and Rajasekharan and Sekhar (1986). They are obtained by using the 12 vectors pointing to the vertices of an icosahedron, which are generated by cyclic permutations of  $(q_x, q_y, q_z) = (\pm 1, \pm \tau, 0)$  where  $\mathbf{q}$  is the wave vector transfer and  $\tau$  is the golden ratio  $(1 + \sqrt{5})/2 = 1.618$ . The allowed values of  $|\mathbf{q}|/|\mathbf{q}_{\max}|$  and the number of the independent  $q_s$  with this magnitude in the vertex model are given in table 1,



**Figure 3.** Selected area electron diffraction patterns taken from a single grain in rapidly quenched  $\text{Al}_{75}\text{Fe}_{25}$  alloy. The 5, 3 and 2-fold symmetry patterns are clearly seen.



**Figure 4.** Selected area electron diffraction patterns obtained from  $\text{Al}_{75}\text{Fe}_{25}$  rapidly quenched alloy showing the streaks of Bragg intensity. The streaks most probably arise from *T*-phases.

where  $q_{\text{max}}$  is the wave corresponding to the most intense line (Parthasarathy *et al* 1986). The observed *d*-spacings and their identification are given in tables 2, 3 and 4. The approximate intensities of the lines are also given.

The observation of 5, 3, 2-fold axes in the electron diffraction pictures is in agreement with the expectations from a quasicrystal. In particular the fact that rotations by  $37.4^\circ$  or  $58.3^\circ$  take the 5-fold axis to the 3- or 2-fold axis is as expected from the icosahedral structure. At present it has not been possible to get further information about the

**Table 1.** The relative magnitudes of  $|\mathbf{q}|/|\mathbf{q}_{\max}|$  of the allowed wave vectors transfers and the number of independent  $\mathbf{q}$ s with this magnitude for various orders in the vertex model.

Order	$ \mathbf{q} / \mathbf{q}_{\max} $	$N$
1	1.0000	12
	1.0515	30
2	1.7013	30
	2.0000	12
3	0.5628	20
	1.0000	12
	1.4511	60
	1.7920	60
	1.9734	60
	2.3840	20
	2.6055	60
	3.0000	12

**Table 2.** X-ray  $d$ -spacings and the corresponding wave vectors  $|\mathbf{q}| = 2\pi/d \text{ \AA}^{-1}$  obtained for  $\text{Al}_{86}\text{Fe}_{14}$  alloys. The approximate intensities of the lines are also given.

Intensity	$d$ (Å)	$ \mathbf{q} $ ( $\text{\AA}^{-1}$ )	Phase with $(hkl)$	$ \mathbf{q} / \mathbf{q}_{\max} $
VW	1.5070	4.16933	I	1.4418
W	1.6021	3.92184	$\text{Al}_3\text{Fe}_2$	1.3562
VW	1.7379	3.61539	$\text{Al}_5\text{Fe}_2$	1.2502
M	2.0317	3.09258	$\text{Al}_3\text{Fe}$ (004) Al (200)	1.0694
S	2.0684	3.03770	I	1.0505
VS	2.1728	2.89175	I	1.0000
S	2.3448	2.67968	$\text{Al}_3\text{Fe}$ (533) Al (111)	0.9266
W	3.9150	1.60490	I	0.5550

$\text{Al}_5\text{Fe}_2$  phase has monoclinic structure with  $a = 9.91 \text{ \AA}$ ,  $b = 10.811 \text{ \AA}$ ,  $c = 8.824 \text{ \AA}$  and  $\beta = 125^\circ$  (Bradley 1932).  $\text{Al}_3\text{Fe}$  phase has an orthorhombic structure with  $a = 47.43 \text{ \AA}$ ,  $b = 15.45 \text{ \AA}$  and  $c = 8.07 \text{ \AA}$  (Bragg and Taylor 1938).

atomic arrangements from the electron diffraction studies. The x-ray pictures reveal the very characteristic feature that the  $|\mathbf{q}|$  corresponding to the most intense lines bears a ratio of 1:1.05 with the  $|\mathbf{q}|$  of the next intense lines. This feature has been exploited by Sekhar *et al* (1985) to identify the quasicrystalline nature of the samples, even though the electron diffraction gives a direct pictorial view. On the other hand, while the selected area electron diffraction spots give the direct symmetry, the x-ray pictures give information about the quasicrystal as well as the matrix in which the crystallites are embedded. In the present case the quasicrystallites are embedded in the Al and crystals of various Al-Fe compounds, which are clearly seen from our x-ray lines.

**Table 3.** X-ray  $d$ -spacings and the corresponding wave vectors  $|\mathbf{q}| = 2\pi/d \text{ \AA}^{-1}$  obtained for  $\text{Al}_{82}\text{Fe}_{18}$  alloys. The approximate intensities are also given.

Intensity	$d$ (Å)	$ \mathbf{q}  \text{ \AA}^{-1}$	Phase with ( $hkl$ )	$ \mathbf{q} / \mathbf{q}_{\max} $
M	1.4504	4.3320	Al (220)	1.4915
M	1.4877	4.2234	I	1.4541
M	2.0667	3.0402	I	1.0468
S	2.096	2.9977	$\text{Al}_3\text{Fe}$ (622)	1.032
VS	2.1633	2.9044	I	1.0000
M	2.2541	2.7874	$\text{Al}_3\text{Fe}$ (11, 1, 3)	0.9597
M	2.3403	2.6848	Al (111)	
			$\text{Al}_3\text{Fe}$ (533)	0.9244
VW	3.7983	1.6542	I	0.5696

**Table 4.** X-ray  $d$ -spacings and the corresponding wave vectors  $|\mathbf{q}| = 2\pi/d \text{ \AA}^{-1}$  obtained for  $\text{Al}_{75}\text{Fe}_{25}$  alloys. The approximate intensities of the lines are also given.

Intensity	$d$ (Å)	$ \mathbf{q}  \text{ (\AA}^{-1}\text{)}$	Phase with ( $hkl$ )	$ \mathbf{q} / \mathbf{q}_{\max} $
M	1.7930	3.5043	$\text{Al}_3\text{Fe}$ (1204)	1.2129
VW	1.9071	3.2946	$\text{Al}_3\text{Fe}$ (480)	1.1403
			(15, 3, 3)	
VW	2.0300	3.0952	$\text{Al}_3\text{Fe}$ (004)	
			Al (200)	1.0713
M	2.0498	3.0653	$\text{Al}_5\text{Fe}_2$	1.0609
S	2.0700	3.0354	I	1.0506
VS	2.1747	2.8892	I	1.0000
S	2.3471	2.6770	Al (111)	
			$\text{Al}_3\text{Fe}$ (533)	0.9265
VW	3.3514	1.8748	$\text{Al}_3\text{Fe}$ (502)	0.6489
M	3.8557	1.6296	I	0.5640

However it is interesting that these quasicrystals undergo a sharp transformation into the crystalline state under high pressure (Baranidharan *et al* 1985). The electrical resistivity studies in a Bridgman anvil apparatus show that these materials transform into the crystalline phases at pressures of 7.9 GPa ( $\text{Al}_{86}\text{Fe}_{14}$ ), 5.4 GPa ( $\text{Al}_{82}\text{Fe}_{18}$ ) and 10.8 GPa ( $\text{Al}_{75}\text{Fe}_{25}$ ) respectively. Since steatite is used as pressure-transmitting medium, there is a small non-hydrostatic component of the pressure and it is not clear whether the small shear component contributes to the transition. Similar pressure transitions were also observed in Al-Mn quasicrystals (Parthasarathy *et al* 1986a, b).

In the case of the  $\text{Al}_{75}\text{Fe}_{25}$  sample knowing the instrument constants of the electron diffraction pictures, the quasilattice constants have been calculated as 4.57 Å. This value is to be compared with 4.60 Å given for the  $\text{Al}_{86}\text{Mn}_{14}$  quasicrystals (Henley 1985). The most intense x-ray diffraction spots come from atomic planes with a separation of

2.17 Å in the  $\text{Al}_{86}\text{Mn}_{14}$  alloy and in all the three present Al-Fe samples. This probably indicates that the local structure is very similar in both cases.

### Acknowledgements

We thank G N Subbanna and Tate Rao for their help and assistance at various stages of this work. Discussions with Profs A L Mackay, M A Viswamitra, R Pandit, H R Krishnamurthy, S Ramaseshan, K J Rao, S Ranganathan, K Chattopadhyay and V Sashisekaran are gratefully acknowledged. Financial assistance from DRDO scheme, Government of India is also gratefully acknowledged.

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