

QUASI CRYSTALLINE Al-Mn ALLOYS: PRESSURE INDUCED CRYSTALLIZATION AND STRUCTURAL STUDIES

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ABSTRACT

Irreversible, pressure induced, quasicrystal-to-crystal transitions are observed for the first time in melt spun alloys at 4.9 GPa for $\text{Al}_{78}\text{Mn}_{22}$ and 9.3 GPa for $\text{Al}_{86}\text{Mn}_{14}$ by monitoring the electrical resistivities of these alloys as a function of pressure. Electron diffraction and x-ray measurements are used to show that these quasicrystalline phases have icosahedral point group symmetry. The crystalline phases which appear at high pressures are identified as h.c.p. for $\text{Al}_{78}\text{Mn}_{22}$ and orthorhombic for $\text{Al}_{86}\text{Mn}_{14}$.

INTRODUCTION

THE discovery of icosahedral point group symmetry in rapidly solidified alloys of aluminium and manganese by Shechtman, Blech, Gratias and Cahn¹ has led to a series of papers on the remarkable features of these alloys². Some authors³⁻¹¹ attribute the five fold symmetry to the aperiodic quasicrystal nature, whereas others have advocated a multiple twinning model^{2,12}. In this letter we report the first observations of pressure induced quasicrystal-to-crystal transitions in rapidly quenched Al-Mn alloys as seen by monitoring the resistivities as a function of pressure. We also present x-ray and electron diffraction pictures of the alloys in relation to their structure.

Our principal results are as follows:— (1) Rapidly quenched $\text{Al}_{78}\text{Mn}_{22}$ exhibits five fold symmetry similar to those reported in $\text{Al}_{86}\text{Mn}_{14}$ by various authors whose findings we reproduce; (2) $\text{Al}_{78}\text{Mn}_{22}$ and $\text{Al}_{86}\text{Mn}_{14}$ undergo irreversible pressure induced quasicrystal-to-crystal transitions at 4.9 ± 0.4 GPa and 9.3 ± 0.8 GPa respectively; (3) $\text{Al}_{78}\text{Mn}_{22}$ crystallizes into a hexagonal close packed structure like that of the μ phase in the Al-Mn alloys; $\text{Al}_{86}\text{Mn}_{14}$ crystallizes into an orthorhombic structure like that of Al_6Mn ; (4) The resistivity of the samples rise gently with increasing pressure below the transition but drop discontinuously on the transition; (5) The quasicrystalline particles are embedded in a matrix of aluminium and aluminium-manganese crystalline alloys.

The Al-Mn alloy samples were prepared by melt spinning the master alloy ingots prepared from high purity (99.99 at. %) Al and Mn. The specimens were

subjected to quasi-hydrostatic pressures up to 13 GPa using a Bridgman anvil apparatus¹³. The electrical resistance was measured *in situ* by a four lead technique. A Keithley Model 225 constant current source and a Keithley Model 616 electrometer were used with high purity copper leads. The resistivity at room temperature and pressure was measured by the Van der Pauw method. Specimens for transmission electron microscopy were prepared by the standard electrochemical techniques. A JEM 200 CX electron microscope was used. X-ray powder pictures were taken with iron K_α radiation.

Figure 1 shows the selected area electron diffraction patterns of rapidly quenched $\text{Al}_{78}\text{Mn}_{22}$. The five-fold, three-fold and two-fold axes characteristic of icosahedral point group symmetry show up clearly. If the sample is aligned so that the two fold pattern is produced, then the three fold and the two fold patterns are obtained by 37.4° and 58.3° rotations respectively. We get similar patterns with rapidly quenched $\text{Al}_{86}\text{Mn}_{14}$ in agreement with earlier works.

Figure 2 shows the resistance of rapidly quenched $\text{Al}_{78}\text{Mn}_{22}$ and $\text{Al}_{86}\text{Mn}_{14}$ as a function of pressure. The resistivities are normalized to their values at room temperature and atmospheric pressure ($114 \mu\Omega\text{cm}$ for $\text{Al}_{78}\text{Mn}_{22}$ and $160 \mu\Omega\text{cm}$ for $\text{Al}_{86}\text{Mn}_{14}$). We associate the discontinuous jump in resistivity of $\text{Al}_{78}\text{Mn}_{22}$ at 4.9 GPa by a factor of nearly 30 and that of $\text{Al}_{86}\text{Mn}_{14}$ at 9.3 GPa by a factor of 9 with a quasicrystal-to-crystal transition, though this has not been checked by an *in situ* measurement of the structure of the alloys. However, the x-ray pictures of these alloys, as discussed below, before and after the application of

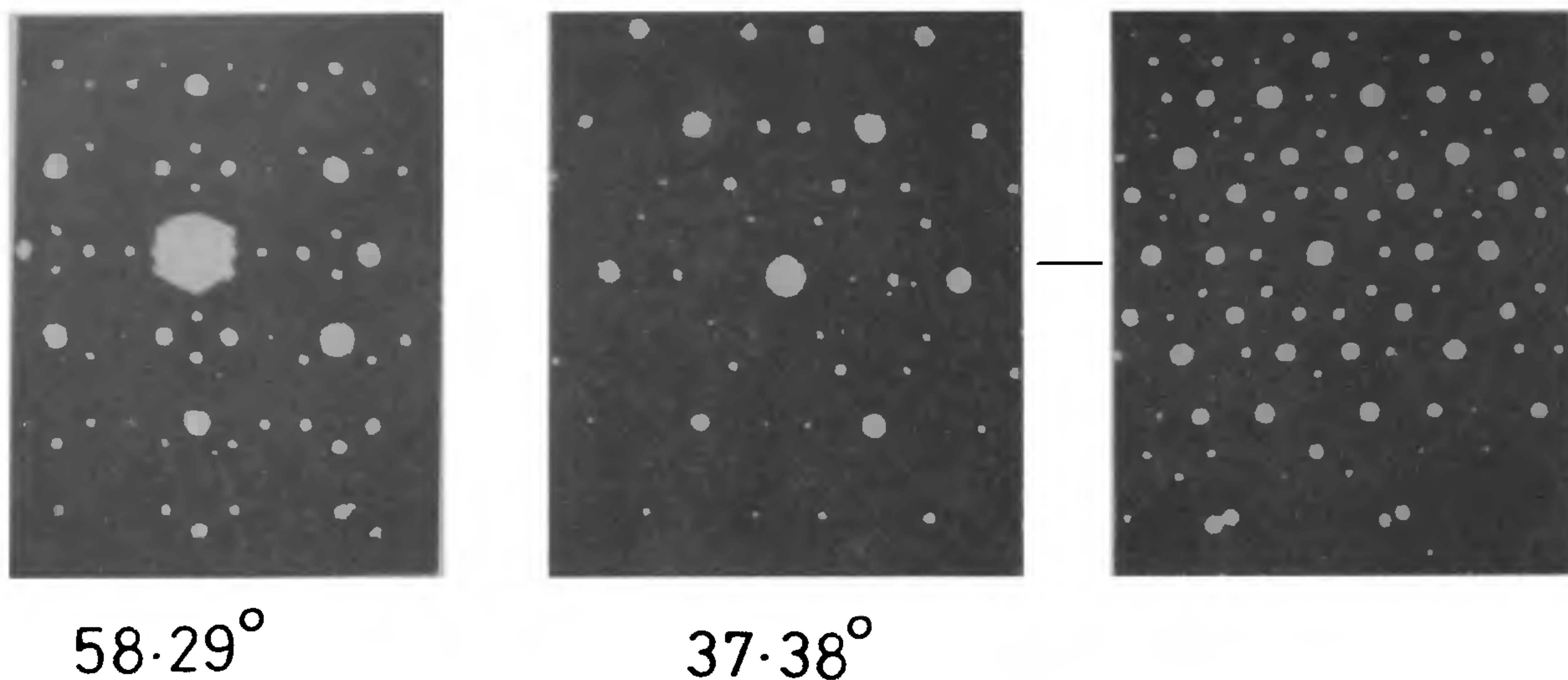


Figure 1. Selected area electron diffraction pattern taken from a single icosahedral grain of rapidly quenched $\text{Al}_{78}\text{Mn}_{22}$ sample. The characteristic 2-fold, 3-fold and 5-fold axes are shown.

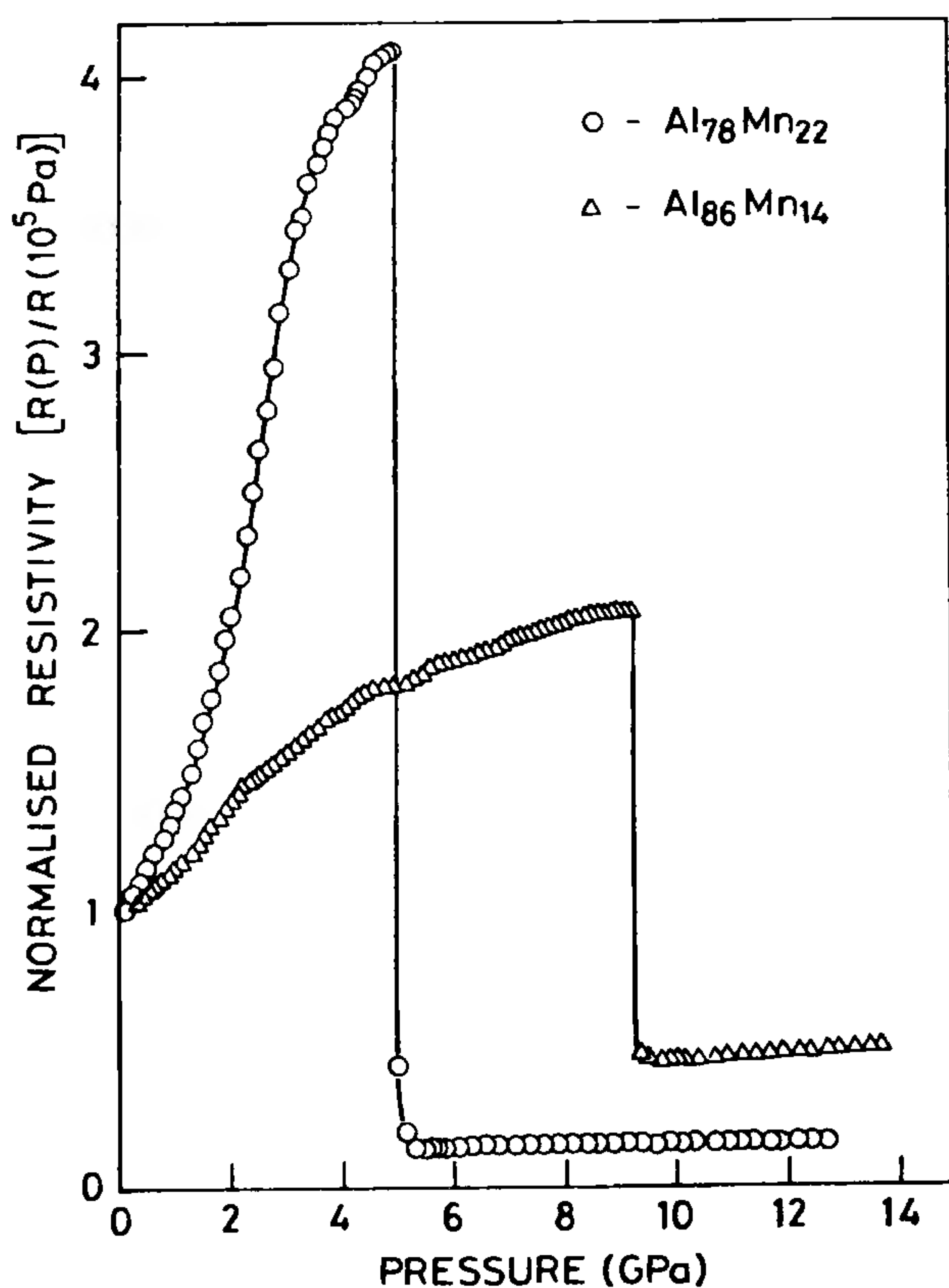


Figure 2. Plot of normalized resistivities of $\text{Al}_{78}\text{Mn}_{22}$ and $\text{Al}_{86}\text{Mn}_{14}$ samples against pressure. The lines through the data points are drawn to guide the eye.

pressure indicate the presence of quasicrystal and crystalline order respectively. The transition is irreversible, which is consistent with the hypothesis that the quasicrystalline phase is metastable¹⁴.

The resistivity of the alloys increases under pressure up to the transition. In contrast the resistivity of the crystalline phase is nearly constant. The initial increase of resistivity with increasing pressure is reminiscent of the behaviour of many metallic glasses¹⁵, where it is conventional to use the Ziman-Faber theory to account for the behaviour. It is not clear to us that the theory will work in quasicrystals whose band structure is complicated. Furthermore, the quasicrystalline fragments of 1–2 microns in size are embedded in a matrix which will have shunting influence which is difficult to estimate.

Figure 3 shows the x-ray powder diffractogram of the pressure induced crystalline phase of $\text{Al}_{78}\text{Mn}_{22}$ and $\text{Al}_{86}\text{Mn}_{14}$. These were taken in a Philips x-ray diffractometer with iron K_{α} -radiation ($\lambda = 1.9373 \text{ \AA}$). The peaks are indexed. The $\text{Al}_{78}\text{Mn}_{22}$ crystallizes into a h.c.p. structure¹⁶ with $a = 19.95 \text{ \AA}$, $c = 24.52 \text{ \AA}$, whereas the $\text{Al}_{86}\text{Mn}_{14}$ crystallizes into an orthorhombic structure¹⁷ with $a = 6.50$, $b = 7.55$ and $c = 8.87 \text{ \AA}$. Both these structures are exactly the same as those of stable phases of alloyed Al and Mn, namely the μ -phase in the case of $\text{Al}_{78}\text{Mn}_{22}$ and Al_6Mn in the case of $\text{Al}_{86}\text{Mn}_{14}$. In particular the (100), (300), (500) etc lines are missing in the powder diffractogram of

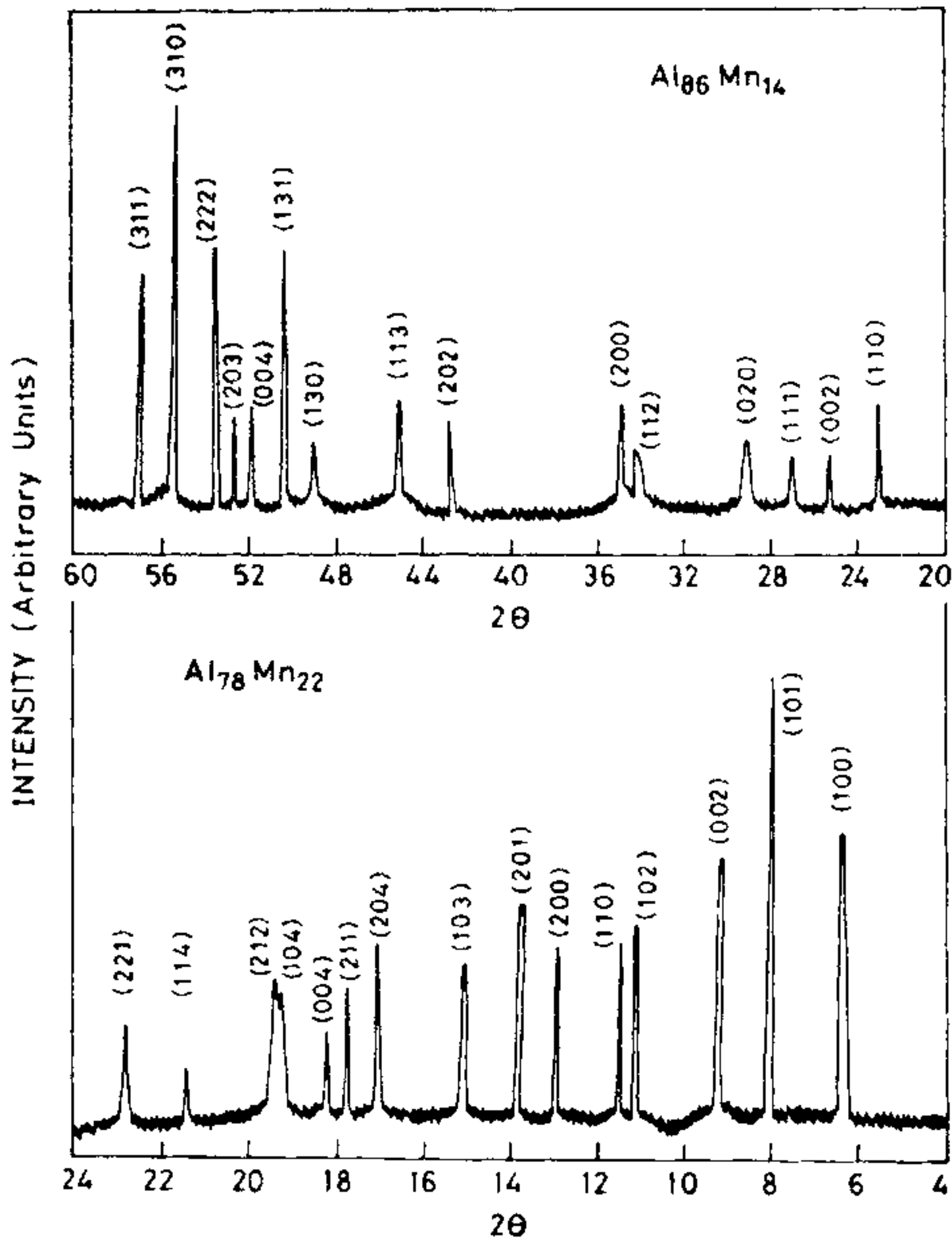


Figure 3. X-ray powder diffractogram of the stable pressure induced crystalline phases of $Al_{86}Mn_{14}$ and $Al_{78}Mn_{22}$. The lines are indexed using the known structures of the equilibrium phases.

crystallized $Al_{86}Mn_{14}$, exactly as the situation for Al_6Mn , because the space group is C_{6mm} . To the best of our knowledge the space group of the μ phase corresponding to 22 at. % Mn in the Al-Mn phase diagram is not known. Any excess aluminium in the material has probably given lines which are buried in the noise of the x-ray diffractogram signal.

The x-ray powder photographs of the quasicrystalline samples yield lines which correspond to the matrix of aluminium and Al-Mn alloys as well as to the icosahedral particles. In order to index the quasicrystal lines, one proceeds as follows. In a simple density wave theory of freezing^{18,19} the wave vector at the most intense peak in the liquid structure factor at freezing equals the magnitude of the basic reciprocal vector set $[G]$. A BCC structure is obtained if the reciprocal vector set $[G]$ consists of the 12 vectors parallel to the edges of a regular octahedron. Quasicrystals with icosahedral point group symmetry can be obtained by

Table 1 Allowed values of wave vector transfer q for various orders in the vertex, edge and face models.

| Order | Vertex Model | | Edge Model | | Face Model | |
|-------|---------------------------|----|---------------------------|----|---------------------------|----|
| | $ \vec{q}/\vec{q}_{max} $ | N | $ \vec{q}/\vec{q}_{max} $ | N | $ \vec{q}/\vec{q}_{max} $ | N |
| 1 | 1.0000 | 12 | 1.0000 | 30 | 1.0000 | 20 |
| | 1.0515 | 30 | 0.6180 | 30 | 0.7136 | 30 |
| | 1.7013 | 30 | 1.1756 | 60 | 1.1547 | 30 |
| | 2.0000 | 12 | 1.4142 | 60 | 1.6330 | 60 |
| | | | 1.6180 | 30 | 1.8683 | 30 |
| 2 | | | 1.7321 | 60 | 2.0000 | 20 |
| | | | 1.9021 | 60 | | |
| | | | 2.0000 | 30 | | |
| | 0.5628 | 20 | | | | |
| | 1.0000 | 12 | | | | |
| 3 | 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

$$|\vec{q}| = \left(\frac{2\pi}{d}\right) \text{ obtained for } Al_{86}Mn_{14} \text{ samples.}$$

| Intensity* | d (Å) | $ \vec{q} (A^{-1})$ | Phase** | $ \vec{q}/\vec{q}_{max} $ |
|------------|-------|---------------------|----------|---------------------------|
| m | 4.94 | 1.27 ₂ | X (110) | |
| w | 4.44 | 1.41 ₅ | X (002) | |
| vw | 3.84 | 1.63 ₆ | I | 0.573 |
| vw | 3.29 | 1.91 ₀ | X (112) | |
| s | 2.62 | 2.39 ₈ | X (202) | |
| s | 2.53 | 2.48 ₃ | X (113) | |
| vs | 2.34 | 2.68 ₅ | Al (111) | |
| vs | 2.20 | 2.85 ₆ | I | 1.000 |
| vs | 2.09 | 3.00 ₆ | II | 1.050 |
| s | 2.03 | 3.09 ₅ | X (311) | |
| m | 2.02 | 3.11 ₀ | Al (200) | |

* vw = very weak; w = weak; m = medium; s = strong; vs = very strong.

** I = Icosahedral phase; X = crystalline Al_6Mn ; indices of the reflections also given.

choosing $[G]$ to be the set of vectors which (a) point to the 12 vertices of a regular icosahedron (vertex model) (b) are parallel to the 30 edges (edge model) or (c) are perpendicular to the 20 faces (face model). All these models lead to sharp diffraction peaks at wave vector transfer $\vec{q} = \sum_i n_i \vec{G}_i$ where n_i is any arbitrary integer and \vec{G}_i is an element of the vector set $[G]$. In table 1 the allowed values of $|\vec{q}|$ and the number N of independent \vec{q} 's with this magnitude are listed for various orders in

Table 3 X-ray d-spacings and corresponding wave vectors q for $Al_{78}Mn_{22}$ samples.

| Intensity* | d(A) | $ q $ (\AA^{-1}) | Phase** | $ q/q_{\max} $ |
|------------|-------|-----------------------------|---------|----------------|
| s | 13.88 | 0.452 ₇ | I' | 1.000 |
| s | 13.22 | 0.473 ₃ | I' | 1.049 |
| m | 8.16 | 0.770 ₀ | I' | 1.701 |
| s | 6.94 | 0.905 ₄ | I' | 2.000 |
| m | 5.69 | 1.10 ₄ | — | — |
| s | 5.33 | 1.17 ₉ | I' | 2.604 |
| m | 4.63 | 1.35 ₇ | I' | 2.998 |
| w | 3.72 | 1.68 ₉ | — | — |
| w | 3.47 | 1.81 ₁ | — | — |
| vs | 2.25 | 2.79 ₃ | I | — |
| vs | 2.09 | 3.00 ₆ | I | — |

* w = weak; m = medium; s = strong; vs = very strong.

** I, I' = Icosahedral phases.

the vertex, edge and face models. In this table one has normalized $|q|$ by taking the first order peak as $|q_{\max}| = 1$ since this will be the most intense peak. The quantity $2\pi/|q|$ is denoted as the d-spacing.

The observed d-spacings of the x-ray lines are given in tables 2 and 3 along with the approximate intensities. The lines are explainable as combination of Al, Al_6Mn and quasicrystal lines. The most intense lines of the quasicrystals ($d = 13.88 \text{ \AA}$ in the case of $Al_{78}Mn_{22}$ and $d = 2.20 \text{ \AA}$ in the case of $Al_{86}Mn_{14}$ quasicrystals) bear a ratio of $1:1.05 \pm 0.01$ with the next intense line. If they are interpreted as the diffraction corresponding to the basic and the smallest second order q vector of the vertex model of a quasi-crystal, their ratio should be 1.0515, as in table 1. The third intense line bears a ratio 1.70 ± 0.02 which is to be compared with the theoretical value of 1.7013. These features enable one to conclude that the vertex model gives a good account of the icosahedral lines. More detailed indexing schemes based on 6 index symbols have been discussed by Elser²⁰ and Bancel *et al*²¹. It is however not yet possible to get any information about the atomic positions in the quasicrystals. It is also noted that our earlier experiments with the Philips Powder Diffractometer gave misleading information because some weak lines were not recorded even with the slowest scan rate.

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