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One-dimensionally modulated quasicrystal phase related to icosahedral Al–Mn–Pd

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ABSTRACT

A new one-dimensionally modulated quasicrystal phase related to the icosahedral Al–Mn–Pd quasicrystal is described from an alloy with composition $Al_{69\cdot8}Mn_{8\cdot3}Pd_{21\cdot9}$ annealed at temperatures between 550 and 715°C and subsequently quenched in water. Systematic tilting experiments reveal that this phase is an icosahedral quasicrystal with a modulation along one of its threefold symmetry axes. It therefore has a trigonal-symmetric Fourier spectrum and a modulation period along the unique threefold axis which corresponds to 15·7 nm. This long-range ordered phase is related to the usual F-type icosahedral quasicrystal as well as to the F2 icosahedral quasicrystal which has a P-type icosahedral lattice.

§ 1. INTRODUCTION

The stable F-type icosahedral quasicrystals are commonly termed 'perfect' icosahedral phases since they exhibit Bragg peaks whose width is resolution limited. This terminology does, of course, not directly imply that these phases are perfectly quasiperiodic; it is also possible that they are additionally stabilized by a contribution of the configurational entropy as has been suggested in the discussions on random tiling models (Elser 1996, Henley 1987, 1991). These 'perfect' icosahedral phases have so far been observed in the following systems: Al–Cu–(Fe, Ru, Os) (Tsai, Inoue and Masumoto 1987, 1988), Al–Pd–(Mn, Re) (Tsai, Inoue, Yokoyama and Masumoto 1990, Beeli, Nissen and Robadey 1991) and Zn–Mg–RE (RE = Dy, Er, Gd, Ho, Tb or Y) (Luo, Zhang, Tang and Zhao 1993).

Ishimasa and Mori (1992) discovered, in contrast with what is known from the Al–Cu–Fe system, that icosahedral Al–Mn–Pd forms various superlattice-ordered phases annealing at low temperatures around 600°C. This phenomenon is very different from the transformations observed for the icosahedral phase in the Al–Cu–Fe system (Bancel 1993). In addition, the ordered phases in the Al–Mn–Pd system have even higher structural perfection than the usual F-type icosahedral phase. The phase diagram of the ternary Al–Mn–Pd system in the region of the quasicrystalline phases (icosahedral and decagonal phases) has been published recently by Gödecke and Lück (1995) as well as by Gödecke, Lück and Beeli (1995).

In a recent publication, Ishimasa (1995a) has shown that one of the new low-temperature phases, called the F2-phase by Ishimasa and Mori (1992) is actually a P-type icosahedral phase (cf. Cahn, Shechtman and Gratias (1986)) with a quasilattice parameter larger by a factor of $\tau(=(1+5^{1/2})/2)$ compared with the F-type Al–Mn–

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Pd icosahedral phase. The occurrence of the F2-phase has been confirmed by Audier, Durand-Charre and DeBoissieu (1993).

In addition to the complicated diffraction patterns found for the superlattice ordered F2-phase, an even more complicated electron diffraction pattern was observed by Ishimasa and Mori (1992) at 705° C, that is at intermediate annealing temperatures (fig. 1 (*b*) in their paper). This type of diffraction pattern was reported to include additional reflections and diffuse streaks along the threefold axes, compared with the diffraction patterns of the P-type low-temperature phase (F2-phase). Obviously, the observation of such long-range ordered phases at low temperatures has important implications in the discussion on the stabilization mechanism of the icosahedral phase in this system. Recently, a new investigation appeared on the influence of specimen composition on the formation of different low-temperature phases in the Al–Mn–Pd system (Ishimasa 1995b).

Since detailed crystallographic and chemical data on the 'intermediate' phase are still missing, the present contribution is intended to provide new structural information on this intermediate phase (abbreviated F*-phase in this paper) as well as information on the conditions of its formation.

§ 2. Experimental details

The specimen has been synthesized in an arc furnace starting from element materials having a purity of at least 99·9% Subsequently, the ingot was annealed at 800° C for 2 days and quenched in water. In a second heat treatment the specimen was annealed at 715° C for 4 days and quenched in water. The same specimen has also been annealed at 700° C for 2 days, at 650° C for 8 days and finally for 9 days at 550° C. The composition was measured by quantitative X-ray microanalysis (wavelength-dispersive spectroscopy) and corresponds to $Al_{69\cdot8}Mn_{8\cdot3}Pd_{21\cdot9}$.

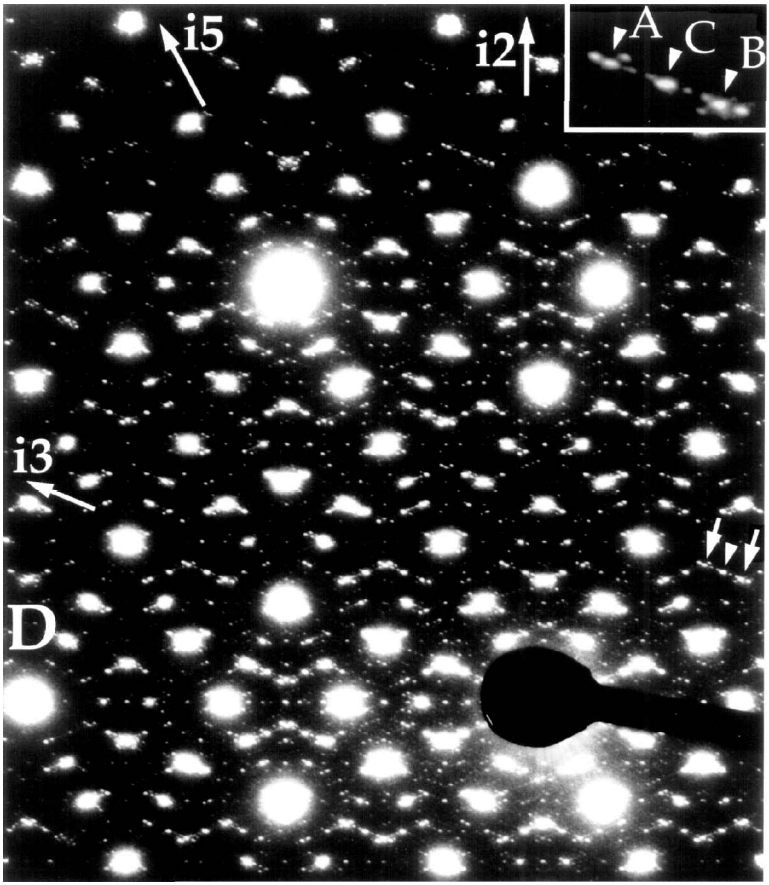
For transmission electron microscopy (TEM), fragments were crushed in ethanol and the microscopic grains were dispersed on a carbon holey foil supported by a standard microscopic copper grid. A Philips CM30ST was used for TEM observation; this instrument was equipped with double-tilt goniometer permitting a tilting range of ±25° and ±15°, respectively. Selected-area electron diffraction (SAD) patterns were obtained with an aperture corresponding to a diameter of 4·6 μm. Additional SAD patterns were obtained with a 200 kV Hitachi HF-2000 FEG transmission electron microscope.

§ 3. Results

All the specimens annealed between 550 and 715° C consisted of a mixture of the F*-phase and the F2-phase, as was evident from twofold SAD patterns. The samples annealed at 715° C or at lower temperatures mainly consisted of the F*-phase, while at 750° C (or higher) the usual F-type icosahedral phase was the only phase observed. The following observations on the F*-phase have all been made on the sample annealed at 715° C, with the exception of fig. 1, which was obtained from the sample annealed at 550° C.

In fig. 1 a twofold SAD pattern is shown which is similar to the SAD pattern in fig. 1 (*b*) of the paper by Ishimasa and Mori (1992). Groups of nine equidistant superlattice reflections parallel to the threefold axes can be recognized. Two basic reflections of the F-type Al–Mn–Pd are indicated by white arrows, while the F2 superlattice reflection half-way between them is indicated by a white arrowhead. The region near these reflections is shown in larger magnification in the inset of

Fig. 1



Typical twofold SAD pattern of the F^* phase. The inset shows a detail, magnified three times, of a group of nine reflections indicated by arrows in the SAD pattern. The reflections labelled A, B and C are from the F2-phase reported by Ishimasa and Mori (1992) and have indices: A, (2/4, 4/2, 0/0); B, (4/4, 0/4, 0/0); C, (3/4, 2/3, 0/0). The strong spot labelled D on the horizontal twofold axis corresponds to 2·05A.

fig. 1. These spots can be indexed (Ishimasa 1995a) as follows: A, (2/4, 4/2, 0/0); B, (4/4, 0/4, 0/0); C, (3/4, 2/3, 0/0). These indices are in accordance with the system of indexing proposed by Cahn *et al.* (1986). The extinction rules, listed by Cahn *et al.* (1986), show immediately that A and B belong to an F-type lattice, while C is a reflection from a P-type icosahedral lattice. This is in agreement with the description given by Ishimasa (1995a).

The following description of the superlattice reflections of the F^*-phase will refer to the basic pattern of the F2-phase. In the image detail shown as inset of fig. 1 the additional F^*-phase reflections can be recognized on each side of the three reflections A, B and C of the F2-phase. These superlattice reflections are aligned along one threefold axis of the icosahedral phase. Along the second threefold axis, additional reflections can also be recognized. Between the reflections A and C, two F^* super-

lattice reflections can be recognized which are positioned exactly at one third and two thirds respectively of the distance between A and C. This indicates that, in comparison with the F2-phase, the F*-phase has a threefold superstructure along the threefold axis. This distance from the F2 reflection to the adjacent F* reflection corresponds to a modulation distance of 15·7 nm in real space. Obviously, the F*-phase has to be considered as a long-range ordered structural variant of the F2-phase. However, the intensity of the F* reflections near the basic reflections (A and B) is generally higher than that near a F2 superlattice reflection (C), and the intensities of the two F* superlattice reflections at both ends of a group of nine equidistant reflections are similar to those of the basic reflections. This suggests that the F*-phase is in fact related to both the F-type as well as the F2-type icosahedral phases. It would formally be possible to index the SAD pattern of the F*-phase with integer indices using a quasilattice parameter three times that of the F2-phase (a = 2·088 nm (Ishimasa 1995a)). However, this would result in very many extinct reflections. In addition, the following experiment shows that such an attempt would not be appropriate, since the F*-phase does not show icosahedral symmetry.

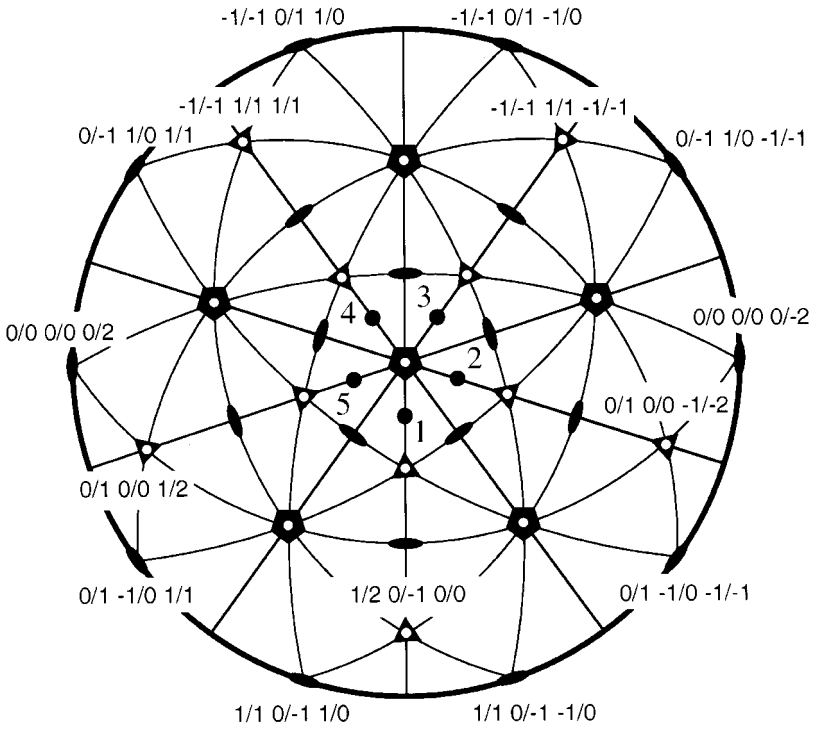
In order to examine the overall symmetry of the F*-phase material we performed the following systematic tilting experiment. The presence of F* superlattice reflections can be verified only if at least one threefold axis is in the plane of the SAD pattern. In order to check on the presence of icosahedral symmetry it was therefore important to observe as many threefold axes of a *single* quasicrystal grain as possible. This has been achieved as described in the next paragraph.

In the immediate vicinity of each fivefold symmetry axis there are five equivalent zones which contain two threefold and one twofold axis in one plane (see fig. 2). These five equivalent zones surrounding the fivefold axis with index (1/0, 0/1, 0/0) have the following indices: (1/1, 1/1, 0/0), (1/ - 1, - 2/1, 1/0), (1/0, 1/1, - 2/1), (1/0, - 1/1, - 2/1) and (- 1/1, 0/1, 1/0). Five different threefold axes can be observed in these five zones. This corresponds to half of all threefold axes of an icosahedral structure. The tilt angle between the central fivefold axis and one of the zone axes measures 13·283°. This is a comparatively small tilt angle which can be reached for appropriate orientations of a quasicrystal, even with the goniometer of a high-resolution objective lens, despite the generally limited tilt range. The schematic drawing in fig. 2 shows the five zone axes in the central part of a stereographic projection with a fivefold axis in the centre. As can be recognized, these special zone axes can be reached from the fivefold zone by rotation around one of the five twofold axes into the direction of the next threefold axis. The result of such an experiment is presented in fig. 3. The SAD pattern along the fivefold axis is shown in fig. 3(*a*), while the five surrounding zone axes are shown in fig 3(*b*). The same indices as in fig. 2 are used to identify the different zones.

The fivefold SAD pattern in fig. 3(*a*) is very similar to that of the F2-phase. Besides the F2 superlattice reflections, additional weak reflections can be recognized near strong Bragg reflections. These additional F* reflections are actually not in the fivefold zone but very close to it in the reciprocal space. A similar effect has been noted for the F2-phase (Ishimasa 1995a). A closer inspection of the weaker reflections in fig. 3(*a*) reveals a break of the fivefold symmetric details.

The zone (1/1, 1/1, 0/0) has F* reflections along both threefold axes (fig. 3(*b*), 1), while the two adjacent zones show F* reflections along one threefold axis only. By contrast, the two zones (1/0, 1/1, - 2/1) and (1/0, - 1/1, - 2/1) show no F* reflections. Similar observations have been made for other quasicrystal grains. It is evident

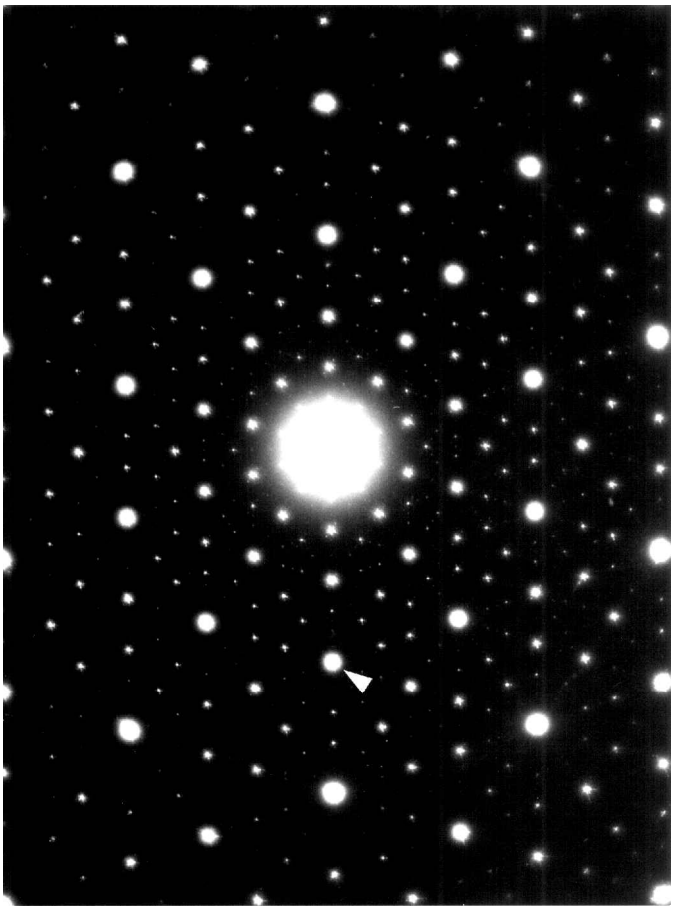
Fig. 2



Stereographic projection of the principal symmetry directions of the icosahedral point group. The five zones marked by a filled circle surrounding the central fivefold axis have been used to obtain the SAD patterns shown in figs. 3 (*b*). Only those threefold and twofold axes which lie within these five zones have been indexed in this stereographic projection.

that the F^*-phase does not have a Fourier spectrum with icosahedral symmetry. The results are schematically presented in the central part of fig. 3 (*b*). The threefold axes with F^* reflections are outlined, while the twofold axis in each zone has been indicated as a thick line. From this figure it is evident that F^* reflections are present along only two of the five threefold axes. Additionally, it has been noticed that a twofold SAD pattern, similar to that shown in fig. 1, changes into a SAD pattern with the modulation along only one of the threefold axes, if the SAD aperture is appropriately displaced on the quasicrystal grain. Since not all threefold axes show the additional reflections, it can be concluded that the F^*-phase is actually a quasicrystal phase which is modulated along one dimension only. The point symmetry of this quasicrystalline phase is trigonal. The results of the experiment shown in fig. 3 can be explained if we assume that the SAD patterns have been obtained from two different domains of the F^*-phase, which have the same modulation along two different threefold axes. Since an aperture of 4·6 μm has been used to obtain the SAD patterns in the experiment, it can be assumed that the typical domain size of the F^*-phase in our specimen is of the order of 2 μm.

Fig. 3

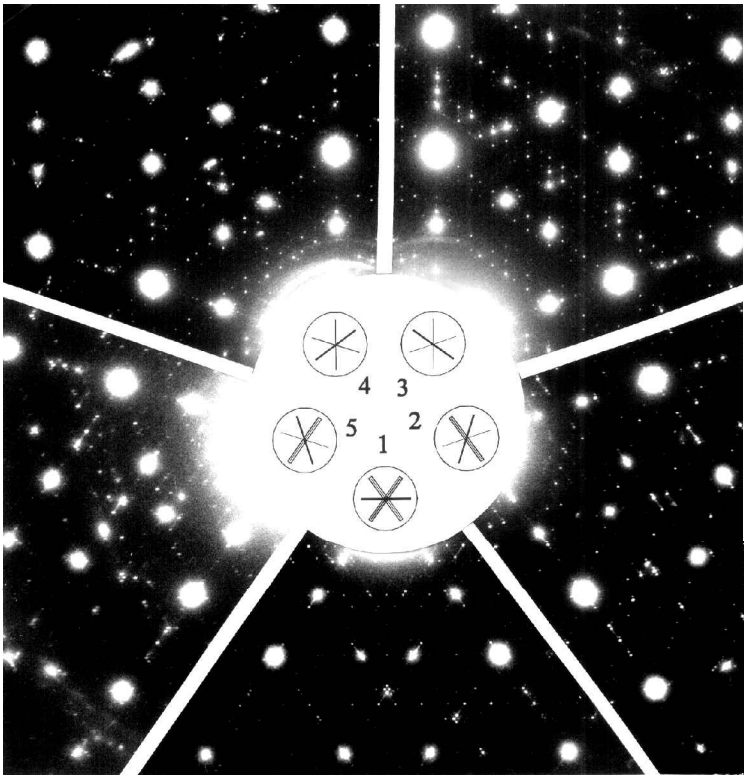


(*a*)

§ 4. Discussion

In a specimen with composition $Al_{69\cdot8}Mn_{8\cdot3}Pd_{21\cdot9}$ we have observed the following phases in quenched samples annealed at different temperatures. At high temperatures (above 750°C) the F-type icosahedral phase is present, while in the temperature interval of 550°C to 715°C the F*-phase as well as the F2-phase occur. This indicates that the F*-phase is formed at an intermediate temperature and, in this specimen, coexists with the F2-phase. In an $Al_{71\cdot0}Mn_{8\cdot0}Pd_{21\cdot0}$ alloy annealed at 600°C, Ishimasa (1995b) exclusively observed the F2-phase whereas, in an $Al_{70\cdot4}Mn_{8\cdot2}Pd_{21\cdot4}$ single-quasicrystal specimen annealed at 600°C, only the F-type icosahedral phase was observed (Capitan, *et al.* 1995).

These observations indicate that at low temperatures (around 600°C) at least three modifications of the icosahedral phase exist which have a composition difference of less than 1 at.%. However, the new experimental evidence presented here clearly shows that the F*-phase does not have icosahedral symmetry; it is a one-dimensionally modulated quasicrystalline phase with trigonal, that is reduced, point



(*b*)

(*a*) Fivefold SAD pattern (1/0, 0/1, 0/0). The spot indicated with a white arrowhead corresponds to 3·31 Å. (*b*) Five SAD patterns with the following indices: 1, (1/1, 1/1, 0/0); 2, (- 1/ - 1, - 2/1, 1/0): 3, (1/0, 1/1, - 2/); 4, (1/0, - 1/1, - 2/1); and 5, (- 1/1, 0/1, 1/0). The schematic drawing in the central part summarizes the results: threefold axes with F^*-phase reflections are outlined, while twofold axes are indicated as thick lines.

symmetry. Since we have studied quenched samples only, it remains possible that the F^*-phase is actually an icosahedrally symmetric phase which, dependent in the quenching process applied, transforms into a one-dimensionally modulated phase. Whether or not this is the case can be clarified by additional *in-situ* experiments with a heating holder. Such experiments are not easy to perform, since commercially available heating holders do not allow the temperature to be measured directly at the specimen position and with high precision. Nevertheless, it appears probable that the F^*-phase is stable even at temperatures below 550° C.

The individual domains with different directions of the one-dimensional modulation are rather small (approximately 2 μm). Therefore it should be emphasized that SAD patterns with a rather small aperture are necessary for the observation of a symmetry break of the icosahedral symmetry. Diffraction patterns from a large area would indicate icosahedral symmetry. For the same reason it is not possible to verify the trigonal symmetry of the F^*-phase by X-ray diffraction as long as one cannot produce single crystals of this new phase.

§ 5. Conclusions

The investigation by SAD techniques reveals details about the formation of the F*-phase, in an $Al_{69\cdot8}Mn_{8\cdot3}Pd_{21\cdot9}$ alloy. It forms from the icosahedral F-type high-temperature phase and coexists at temperatures of 550–715° C with the F-type as well as the F2-type low-temperature phases. Systematic tilting experiments lead to the conclusion that the F*-phase is a one-dimensionally modulated quasicrystalline phase with trigonal symmetry. The modulation period corresponds to 15·7 nm. It remains an open question whether the F*-phase actually has icosahedral symmetry, whereby the observed lower symmetry would be due to a transformation during the quenching process from the higher temperature. However, judged on the basis of the data available at present, it appears likely that the F*-phase is one of the thermodynamically stable quasicrystal phases in the Al–Mn–Pd system.

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