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T. Motsch, F. Dénoyer, P. Launois, M. Lambert. Icosahedral non-quasicrystalline Al-Cu-Fe. Journal de Physique I, 1992, 2 (6), pp.861-870. 10.1051/jp1:1992184 . jpa-00246607

HAL Id: jpa-00246607

<https://hal.science/jpa-00246607>

Submitted on 1 Jan 1992

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Classification
Physics Abstracts
61.55H

Icosahedral non-quasicrystalline Al-Cu-Fe

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(Received 26 July 1991, revised 28 November 1991, accepted 7 February 1992)

Résumé. — Nous présentons des diagrammes de diffraction de rayons X obtenus à l'aide de la méthode de précession, par un alliage $\text{Al}_{63.5}\text{Cu}_{24}\text{Fe}_{12.5}$ de symétrie icosaédrique [1]. Toutes les positions des pics de diffraction sont interprétées au travers d'un modèle très simple de microcristal, dans lequel des domaines cristallins cohérents ont des relations d'orientation particulières afin de restituer la symétrie icosaédrique sur les clichés de diffraction. Un modèle de quasicristal dans lequel des champs de phasons auraient été introduits est aussi évoqué.

Abstract. — X-ray « single » crystal precession photographs of an $\text{Al}_{63.5}\text{Cu}_{24}\text{Fe}_{12.5}$ alloy of icosahedral symmetry are presented [1]. All the diffraction peak positions are interpreted within the framework of a very simple microcrystalline model in which coherent crystalline domains having particular orientational relationships restore the icosahedral symmetry on diffraction patterns. A quasicrystalline model in which phason fields are introduced is also discussed.

1. Introduction.

Since the original discovery of an icosahedral phase in rapidly quenched alloys of Al-Mn [2], icosahedral phases have been found in many others intermetallic alloys. The diffraction patterns of *perfect* quasicrystalline phases are consistent with the icosahedral point group; due to the perfect coherence of the quasiperiodic order, their diffraction peaks are sharp and their peak positions are given by integer linear combinations of a finite set of six basis vectors. Models for indexing icosahedral structures have been derived from a suitable irrational cut of periodic higher dimensional structures [3]. However, in many cases, diffraction patterns do not simultaneously exhibit all these features and small deviations inconsistent with the perfect quasicrystalline (QC) model are observed. These anomalies such as — small shifts in peak positions from ideal icosahedral positions, — peak broadenings, — anisotropic peak shapes or — multicomponent peaks can break but need not break the point group symmetry. Several interpretations of these deviations have been reported. For symmetry breakings, large unit cell icosahedral approximants [4, 5], obtained from a rational cut in the superspace model or a twinning model [6] have been considered. Phason-type defects have also been introduced in

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the QC model and account for diffraction data presenting or not small deviations from the icosahedral symmetry [7]. Similarities between frozen phason quasicrystals (« strained » QC) and the Pauling twinning model [6] have been discussed in [8].

When the icosahedral symmetry remains unbroken and a « twinning » model is appropriate [9], a pertinent question is : how it is possible to account for the *whole* Al-Cu-Fe X-ray diffraction patterns which exhibit sharp peaks and icosahedral symmetry, but for which peak positions are not understandable using quasicrystallography [1] ? The model we favour is based on the idea of coherent crystalline domains having peculiar orientational relationships. The distribution in orientation of crystalline domains is such that the icosahedral point group is restored on diffraction patterns and the *coherence* of orientational domains is such that the long range order giving sharp peaks is preserved (even if the domain size is small) [9c]. This model is termed a microcrystalline (MC) model. It has been naturally suggested from an interpretation of HREM images [10] and can account for the peak positions from (icosahedral) symmetry axes in diffraction experiments [1]. The purpose of this paper is to demonstrate that such a *simple model* can explain the *whole* X-ray diffraction patterns obtained from a dodecahedral particle of $\text{Al}_{63.5}\text{Cu}_{24}\text{Fe}_{12.5}$. A comparison with a strained QC model is also made.

2. X-ray result analysis.

The preparation of samples used in this investigation has been described previously in [1]. Figure 1 shows the Buerger monochromatic X-ray diffraction patterns from $\text{Al}_{63.5}\text{Cu}_{24}\text{Fe}_{12.5}$ particles taken from reference [1]. By taking photographs with long exposure times an intensity ratio of $\sim 10^4$ could be obtained between the strongest and the weakest diffraction peaks. This ratio was determined by taking photographs of various durations i.e. ~ 200 -20-2 h and 12 min. Due to the method of selection of reciprocal plane, there is an experimental « width » in the direction perpendicular to the selected plane ; for our experimental conditions, this « width » is estimated to about $0.0125 \text{ \AA}^{-1}$.

Schematics of the peak positions in the top right hand quadrants of figures 1a, 1b and 1c are shown in figures 2a, 2b and 2c respectively. These diffraction data can now be analyzed in terms of a microcrystalline icosahedral model. In this model we assume :

- i) the existence of *coherent* crystalline domains having orientational relationships which restore the forbidden crystallographic symmetry in diffraction patterns [1, 9c] ;
- ii) that crystalline domains are tiled periodically with a primitive rhombohedral unit cell of parameters $r = 32.08 \text{ \AA}$ and $\alpha = 36^\circ$ [1, 10].

To obtain the icosahedral symmetry $m\bar{3}5$, ten orientations of the rhombohedral subgroup $\bar{3}m$ are necessary [1, 11]. The insets of figures 3a, 3b, 3c are schematics of these ten domain orientations seen along the 3-fold, 5-fold and 2-fold axes respectively. Within this description, diffraction peaks are always sharp Bragg peaks, because of the coherence of orientational domains, even if the sample consist of a great number of small domains.

As far as *peak positions* are concerned, the diffraction patterns can be calculated by superimposing the reciprocal lattices of the ten rotated domains. Calculations have been made for « zero-level » reciprocal planes perpendicular to the 3-, 5- and 2-fold axes. As mentioned above, in order to fit our calculations with experimental results, we need to take into account resolution effects perpendicular to the reciprocal plane, which are usually not considered : numerical calculations have been made using a window of width Δ centered on each zero-level ideal reciprocal plane.

The results are identical for $\Delta = 0.0001 \text{ \AA}^{-1}$ and $\Delta = 0.001 \text{ \AA}^{-1}$ and are exhibited in figures 3a, b and c, for the zero level reciprocal planes respectively perpendicular to a 3-, 5-

Fig. 1. — Monochromatic X-ray precession diffraction patterns, from reference [1], obtained with an incident beam wavelength $\lambda = 1.542 \text{ \AA}$ ($\text{CuK}\alpha$ radiation) for « zero-level » reciprocal planes with successively 3-, 5-, 2-fold axes (a, b, c) parallel to the precession axis. The exposure time is 200 h. $\text{CuK}\alpha$ radiation has been selected using the (002) reflection of a pyrolytic graphite monochromator.

and 2-fold axis. With so small a window width, the numerical calculations give the theoretical (i.e. without width) reciprocal equatorial planes without any additional spot and the peak positions can be simply deduced using symmetry arguments.

— If we first consider the peak positions of figure 3a, apart from some of those on the two-fold axes (2 on the pattern), all the diffraction spots arise from one single periodic domain orientation (1 in the inset of Fig. 3a); their positions are periodic and can be described by an

Fig. 2. — Peak positions obtained from diffraction patterns (Figs. 1a, b, c). They are taken in order to simulate anisotropic shapes. Diffraction patterns exhibit a few peaks of low intensity corresponding to contamination by harmonics ($\lambda/2$ and $\lambda/3$); these diffraction peaks have been suppressed in the peak position measurements.

hexagonal reciprocal lattice : the unit cell of parameter $b^* = (1/9.913) \text{\AA}^{-1}$ is shown in figure 3a (this 9.913 $\text{\AA}$ value corresponds to interplanar spacings d_{110} or d_{101}).

— The situation is quite different in figure 3b since for this orientation, perpendicular to a 5-fold axis, the ten domain orientations (1-10 in the inset of Fig. 3b) all contribute to the diffraction pattern and the peak positions result from the superimposition of five rotated rhombic reciprocal lattices, with a rhombus edge $a^* = (1/16.040) \text{\AA}^{-1}$ and angle 72° (the 16.040 $\text{\AA}$ value corresponds to the interplanar spacings d_{110} , d_{101} or d_{011}).

— Along the two-fold axes (denoted by 2 in Fig. 3), two incommensurate reciprocal periodicities with periods a^* and b^* ($b^*/a^* = \tau$, the golden mean) are superimposed. This is

Fig. 3. — Calculated zero level reciprocal planes perpendicular to 3-fold (a), 5-fold (b), 2-fold (c) axes, using a width $\Delta = 0.001 \text{ \AA}^{-1}$. The insets are schematics of the ten domain orientations projected onto planes perpendicular to the different symmetry axes. Note that the corresponding polyhedron is the stellation of [10]; it is only indicative of domain orientations and has no particular physical meaning.

easily seen in figure 3b where four domain orientations contribute to the diffraction peaks along the 2-fold axes: for example, for the two-fold axis parallel to the q_k axis, the spots corresponding to the a^* periodicity come together from domain orientations 3 and 4 and the peaks attributed to the b^* periodicity arise from domain orientations 1 and 6.

— The same arguments can be developed to explain the diffraction pattern of figure 3c. Here again, the ten domain orientations all contribute. For the two-fold axes along

q_h (or q_k), the diffraction peaks corresponding to the a^* periodicity come from domain orientations 5 and 6 (or 1 and 2), whereas the spots corresponding to the b^* periodicity arise from domain orientations 1 and 2 (or 3 and 8). The diffraction peaks along the ternary axes (3 and 3' in Fig. 3c) come from one single domain orientation (5 and 6 respectively); the spots are periodic along this direction with the $c^* = (1/29.968) \text{ \AA}^{-1}$ periodicity (the 29.968 Å value corresponds to the d_{111} interplanar spacing). Similarly, five domain orientations (1, 2, 4, 5, 9 or 1, 2, 6, 7, 10) contribute to the diffraction peaks along the 5-fold axes (noted 5 or 5' in Fig. 3c), and these peak positions are periodic with the periodicity $d^* = (1/16.865) \text{ \AA}^{-1}$, the 16.865 Å value corresponding to the d_{100} interplanar spacing. Apart from the two-fold axis q_k , the peak positions of the whole diffraction pattern can be interpreted as arising from the superimposition of the three reciprocal lattices constructed from the cells drawn in figure 3c: a rhombus cell of parameter d^* and 116.58° angle, and two oblique cells with parameters a^* , c^* and a 69.09° angle and a 110.91° angle respectively. This leads to a lattice of periodic lines parallel to the q_h direction.

To illustrate now the influence of the experimental resolution, the calculated modifications of a « zero-level » reciprocal plane are represented in figure 4 for different Δ values of the window width. These patterns show how the diffraction pattern is filling up, and in particular it is interesting to discover how multicomponent peaks are constructing (spots arrowed in Figs. 4a, 4b and 4c). Figures 5a, 5b and 5c then make the comparison between the calculated « zero-level » reciprocal planes using a window width equal to the experimental resolution and the respective measured diffraction planes: the overall features of the diffraction patterns are reproduced well when Δ is taken equal to $0.0125 \text{ \AA}^{-1}$. These results demonstrate the validity of the MC model used in the interpretation of the diffraction patterns in an Al-Cu-Fe alloy.

Although the aim of this paper is not to describe the internal structure of each twin variant (i.e. positions of atoms in the unit cell), some considerations about the *peak intensities* can be made. Since all measured strongest peak « mean » positions correspond to small $Q_\perp$ peaks within the scope of a quasicrystalline model (cf. also Tab. I of Ref. [1]), the unit cell decoration is certainly of the approximant type. Moreover, for such a decoration of a rather large unit cell, the existence of numerous calculated diffraction peaks for which the intensity is too small to be measured is not at all surprising.

3. Discussion.

If we consider the strongest peaks, we observe that they exhibit an anisotropic shape. Within the framework of the microcrystalline model, this is because of the juxtaposition of several peaks with nearly the same wave-vector in modulus coming from the rotated domains (see for example Fig. 4). In the case of a perfect QC description, this kind of « peak shape » does not exist [3]: we think that they cannot be explained even by taking into account the resolution width perpendicular to the diffraction planes, because of a minimum distance between intense QC peaks [12]. However, it is also tempting to analyze our data within the scope of a QC model in which phason fields are introduced [7, 11, 14]. Indeed, from the geometrical and group theory points of view, descriptions of the Al-Cu-Fe MC state in a 6-D superspace with phason fields are possible [11, 14]; nevertheless, the 3-D MC model is easier to use when indexing diffraction patterns. Moreover, if one links the physical meaning of a frozen-in disorder to phason fields, Al-Cu-Fe does not seem to be a good candidate for a phason field description, and is instead described better by the 3-D MC model. Specifically: i) the sharpness of diffraction peaks indicates that phason fields should be linear and not quadratic [7], a strong constraint, whereas coherence between domains in the MC model explains simply the peak sharpnesses, as has already been found in more « classical » twinned systems,

Fig. 4. — Effect of resolution in precession experiments for the zero-level reciprocal plane perpendicular to a 3-fold axis: arrows show the multiple components of selected diffraction peaks; these components arise from differently orientated microcrystalline domains and not from higher order Laue zones [4].

ii) as discussed in [8], a criterion favouring a QC with phason fields description over that of a twinned model should be that « different samples of the same material can exhibit different diffraction peak shifts ». This is not the case here. Different Al-Cu-Fe particles taken from the ingot have the *same* diffraction patterns. Furthermore, *in situ* X-ray diffraction patterns recorded as a function of temperature do not exhibit sensitive modifications in the peak positions up to about 700 °C, at which point the quasicrystalline state is recovered. This is a supplementary argument indicating that the MC phase is not a frozen phason quasicrystalline one.

Within the framework of the MC model, the approximant type unit cell decoration implies that the strongest peaks are situated near those of a QC and that orientational relationships between the domains restore perfect icosahedral symmetry in reciprocal space, just as for a

Fig. 5. — Comparison between calculated with a width $\Delta = 0.0125 \text{\AA}^{-1}$ (dots) and measured (small circles) « zero-level » reciprocal planes perpendicular to 3-fold (a), 5-fold (b), 2-fold (c) axes.

perfect quasicrystal. The clear recognition of a microcrystalline state in Al-Cu-Fe from X-ray precession photographs has been possible because the unit cell, although rather large, is small enough so that shifts between measured and predicted QC diffraction peaks are visible. As the unit cell becomes larger, the differences between QC and MC diffraction patterns become smaller, as is found for example in a decagonal Al-Cu-Co-Si alloy [15]. In summary, due to unit cell decoration, there are strong resemblances between MC and QC diffraction patterns and careful analyses, together with complementary experiments and techniques, are often needed to differentiate a QC and a MC.

An open question remains about the domain organization (in « positions »). At the present time no diffraction features indicating a vertex domain organization have been found, but

future experiments, such as small angle ones, are potentially very interesting. For a discussion about this, see [9c, 16].

4. Conclusion.

In spite of strong resemblances with QC diffraction patterns, 5-, 3- and 2-fold azimuthal diffraction planes cannot be indexed in the scope of a QC model whereas complete indexing is achievable within the framework of a MC model. We have laid emphasis upon experimental resolution effects, without which the complete indexing is not possible. Intensity considerations indicate an approximant-type unit cell decoration. Finally, the possible indexing of the data with a QC model including phason strains has been considered, but our conclusion is that the MC model is easier to use and does not need to clarify the physical meaning of frozen-in disorder arising from phason fields.

Acknowledgments.

It is a pleasure to acknowledge J. M. Lang and P. Duroux for the preparation of the Al-Cu-Fe ingot, M. Audier for interesting discussions and D. Petermann for his photograph peak position determination program.

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