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Icosahedral AlCuFe alloys : towards ideal quasicrystals

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Résumé. — Le désordre topologique et l'ordre chimique à grande distance ont été étudiés par diffraction des rayons X sur poudre dans l'alliage i-$Al_{65}Cu_{20}Fe_{15}$ brut de trempe. Le perfectionnement spectaculaire de l'état quasicristallin, obtenu par recuit d'échantillons hypertrempés, a été mesuré quantitativement ; le matériau recuit final correspond aux prévisions théoriques du modèle quasicristallin idéal dans les limites de la résolution instrumentale. Après recuit à 1 073 K, l'alliage de composition nominale $Al_{65}Cu_{20}Fe_{15}$ est biphasé. La composition $Al_{63}Cu_{25}Fe_{12}$ conduit quant à elle à une structure icosaédrique monophasée qui convient à l'analyse par diffraction des rayons X ou des neutrons sur un mono quasi-cristal.

Abstract. — The topological and chemical long range orders in the icosahedral $Al_{65}Cu_{20}Fe_{15}$ alloy have been studied by X-ray powder diffraction. The spectacular enhancement of the quasicrystalline state by annealing of rapidly quenched samples have been quantitatively measured showing that the final annealed product fits the theoretical predictions of the ideal quasicrystal model within the instrument resolution. Whereas, after annealing at 1 073 K, $Al_{65}Cu_{20}Fe_{15}$ is two-phased — that makes difficult any fine study of the structure and the properties of the ideal icosahedral phase — a close composition $Al_{63}Cu_{25}Fe_{12}$ leads to a single-phased icosahedral structure suitable for single quasicrystal X-ray and neutron diffraction analysis.

Introduction.

High quality quasicrystal making has been one of the basic topics of research in metallurgy for providing samples suitable for the study of the structural and physical properties of quasicrystals. Most of the available materials are metastable phases issued from rapid quenching and contain an important fraction of topological disorder that obscures the intrinsic quasiperiodic nature of the icosahedral phases. Topological disorder has even been considered as an intrinsic property of these phases after the discovery of the first stable i-AlLiCu [1, 2] and GaMgZn [3] alloys which, initially obtained by rapid quenching, transform by subsequent annealing into a more disordered state.

The announcement, two years ago, by Tsai *et al.* [4] of a new stable icosahedral phase in the $Al_{65}Cu_{20}Fe_{15}$ alloy has been the starting point of an intensive research where it has been shown that this structure can indeed be described as a high quality ordered F-superstructure of the

usual primitive 6D hypercubic lattice [5-7]. X-ray powder spectrum of the rapidly quenched alloy shows peak widths similar to those observed in the other icosahedral phases like AlMnSi [8, 9, 10]. But, contrary to the previous alloys, annealing treatments of as-quenched samples lead to a spectacular narrowing of the peak widths corresponding to an elimination of the as-quenched defects [11, 12].

This paper is devoted to a quantitative X-ray diffraction study of rapidly quenched AlCuFe ternary alloys $Al_{65}Cu_{20}Fe_{15}$ and $Al_{63}Cu_{25}Fe_{12}$ and their evolution towards ideal quasicrystal after annealing. Using this latter composition $Al_{63}Cu_{25}Fe_{12}$, we have succeeded in elaborating a metallurgical process which leads to large single phased quasicrystals suitable for neutron and X-ray single crystal diffraction and physical properties fine measurements.

Experimental.

Master alloys of compositions $Al_{65}Cu_{20}Fe_{15}$ and $Al_{63}Cu_{25}Fe_{12}$ have been prepared from the pure elements (Al : 99.99 %, Cu : 99.99 %, Fe : 99.95 %) by levitation melting in a controlled helium atmosphere. The alloys have been subsequently rapidly quenched by planar flow casting on a copper wheel under a helium atmosphere (quenching temperature : 1 423 K, tangential speed of the wheel : 25 m/s). The flakes were ground and sifted through a 32 μm sieve for powder X-ray diffraction pattern measurements.

High-resolution X-ray experiments have been done using the synchrotron radiation on the line D23 of LURE-DCI, which is equipped with a double-crystal monochromator (Si 111) in the incident beam and an analyzer crystal (Ge 111) in the diffracted beam [13]. The resolution Δq, measured on the (111) Bragg peak from a standard Ni powder sample, was 3×10^{-4} Å^{-1} (the diffraction vector q being defined as $q = 2 \sin \theta / \lambda$).

Due to lack of allocated beam time at the synchrotron source, peak width measurements of the as-quenched samples have been performed on a conventional diffractometer equipped with a curved LiF monochromator in the diffracted beam, using the CuK_β radiation. The resolution was about 2×10^{-3} Å^{-1}. The intrinsic broadening $\Delta\theta$ has been obtained through the Taylor expression [14]

$$\Delta\theta = [(B - b)(B^2 - b^2)^{1/2}]^{1/2}$$

where B is the observed full width at half maximum and b is representative of the instrument broadening. The use of this formula is justified by satisfactory agreement with the high-resolution data.

Integrated intensity measurements have been made taking advantage of the variation in the atomic scattering factors near the absorption edges of Cu and Fe, using the synchrotron radiation and also classical targets (CoK_α and CuK_β radiations).

Results.

1. IDENTIFICATION OF THE PHASES IN THE $Al_{65}Cu_{20}Fe_{15}$ ALLOY.

As quenched. — All the peaks of the X-ray spectrum can be indexed using an icosahedral 6D I-reciprocal lattice with a (primitive) 6D lattice parameter of the icosahedral phase of 6.320 ± 0.008 Å. A few additional weak peaks indicate the presence of a small amount of a simple cubic FeAl-type phase ($a = 2.90$ Å) [7].

Annealed. — After annealing for 30 min at 1 073 K the intensities of the fundamental lines decrease by about 30 %, and the precipitation of a monoclinic Al_3Fe-type phase is observed (Fig. 1). There is no companion decrease in the intensity of the superlattice peaks which implies a significant increase in the chemical long range order parameter of the icosahedral

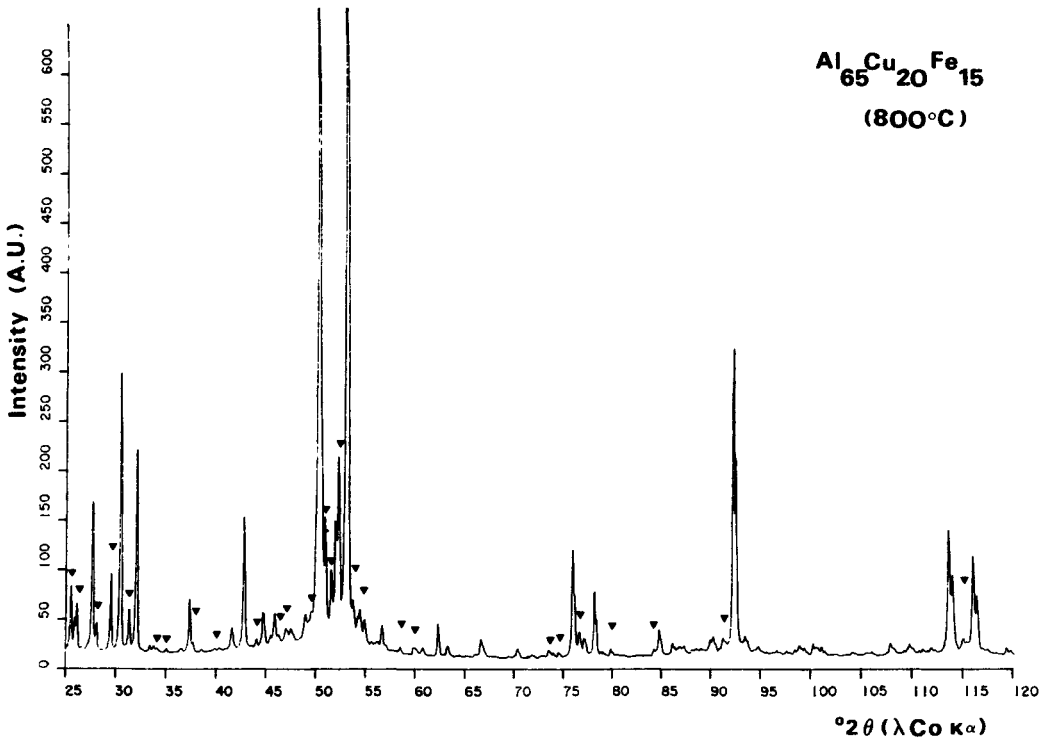

Fig. 1. — X-ray powder diffraction pattern of the $Al_{65}Cu_{20}Fe_{15}$ alloy. The alloy has been quenched by planar flow casting, then the flakes have been annealed for 30 min at 1 073 K ((▼) Al_3Fe-type phase).

phase. Correlatively the (primitive) 6D lattice parameter decreases slightly to $a_6 = 6.3146 \pm 0.004$ Å.

The Al_3Fe compound, as studied by Black [15], has the lattice parameters : $a = 15.489$ Å, $b = 8.083$ Å, $c = 12.476$ Å and $\beta = 107.68°$. The Al_3Fe-type compound we observe has the lattice parameters : $a = 15.535$ Å, $b = 7.993$ Å, $c = 12.509$ Å and $\beta = 107.96°$. These values are similar to those measured by Ishimasa *et al.* [5] in an $Al_{65}Cu_{20}Fe_{15}$ alloy annealed for 65 hours at 1 073 K.

2. TOPOLOGICAL DISORDER IN THE $Al_{65}Cu_{20}Fe_{15}$ ICOSAHEDRAL PHASE. — During the heat-treatment, a considerable increase in the structural perfection of the icosahedral phase occurs which is observed by both a perfectioning in the peak positions and a narrowing in the peak widths of the X-ray powder diffraction spectra (Fig. 2).

2.1 *Displacement from the ideal 6D I reciprocal lattice.* — The indexing of the as-quenched icosahedral phase has been performed in the scheme proposed by Cahn *et al.* [16] with a 6D F-direct lattice parameter $a_F = 6.32 \times 2 = 12.64$ Å. Table I gives the measured peak positions and the deviations ($\Delta q_\parallel$) from those calculated for an ideal quasicrystal. The largest difference reaches 10^{-3} Å^{-1}. These results have been obtained from experiments performed using the CuK_β radiation. In order to check the intrinsic values of $\Delta q_\parallel$ we have done the same measurements for the different experiments performed, using various wavelengths. As shown in figure 3, the different experiments lead to similar values for the observed deviations.

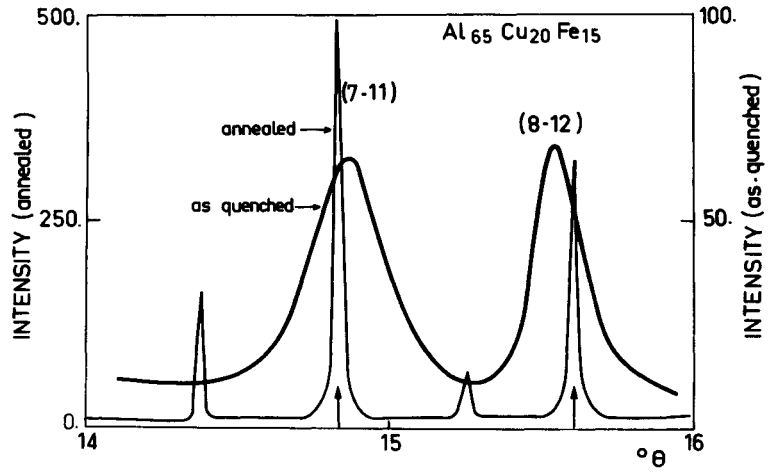

Fig. 2. — Increase in the structural perfection of the icosahedral phase, in an $Al_{65}Cu_{20}Fe_{15}$ sample annealed for 30 min at 1 073 K. The arrows give the calculated positions, for the ideal icosahedral phase (λ = 1.746 Å).

Table I. — *Observed positions of the reflections* ($q_\parallel$), *deviation from the calculated values* ($\Delta q_\parallel$), *and intrinsic peak widths* ($\omega_\parallel$) *for an as-quenched* $Al_{65}Cu_{20}Fe_{15}$ *icosahedral alloy.* (*Experiment performed using the* CuK_β *radiation.*)

Reflection (N, M)	$q_\parallel$ (Å^{-1}) (observed)	$q_\perp$ (Å^{-1}) (calculated)	$\Delta q_\parallel$ ($\times 10^3$, Å^{-1}) q_{calc}-q_{obs}	fwhm ($\omega_\parallel$) ($\times 10^3$, Å^{-1})
(7, 11)	0.29387	0.04274	− 0.356	5.40
(8, 12)	0.30698	0.07271	1.005	3.09
(11, 16)	0.35646	0.10034	0.787	5.95
(14, 21)	0.40831	0.09618	− 0.878	6.98
(15, 23)	0.42571	0.08434	− 0.666	4.05
(18, 29)	0.47348	0.02641	0.470	1.65
(20, 32)	0.49852	0.04494	− 0.178	3.35
(31, 48)	0.61361	0.10994	− 0.442	8.28
(38, 61)	0.68782	0.05212	− 0.090	5.05
(40, 64)	0.70460	0.06355	0.160	3.12
(52, 84)	0.80603	0.02777	0.295	2.51
(70, 113)	0.93544	0.03833	− 0.139	4.05
(72, 116)	0.94773	0.05282	0.168	5.63
(102, 165)	1.12968	0.01486	0.202	4.00
(104, 168)	1.14012	0.03927	0.124	4.88
(136, 220)	1.30452	0.01716	0.150	5.40

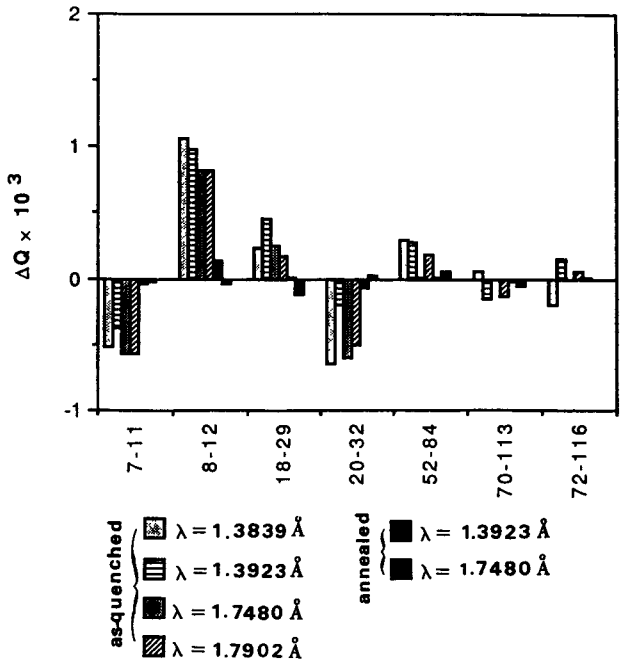

Fig. 3. — Deviations from the theoretical icosahedral positions of the reflections, for the different experiments performed : in the as-quenched state, systematic deviations occur, which are released by annealing.

An annealing at 1 073 K for 30 min leads to drastic changes in the peak positions : although, in the annealed state, only those few peaks which do not superimpose with diffraction lines of the monoclinic Al_3Fe-like phase can be measured with accuracy, the displacements from the expected values decrease by a factor of ten or more and fall within the uncertainty domain of the experimental measure (see Fig. 3).

2.2 *Peak widths.* — Intrinsic peak widths (full width at half maximum : fwhm, noted $\omega_{\parallel}$), measured on as-quenched samples, are given in table I and have been plotted according to two possible types of disorder suggested by Horn *et al.* [17] : icosahedral glass (Fig. 4) and frozen-in phason strain (Fig. 5).

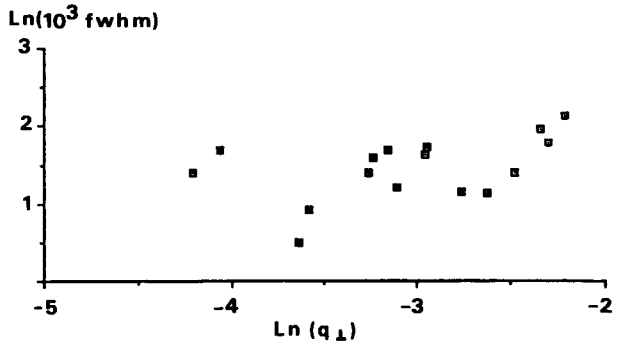

Fig. 4. — Icosahedral glass model : plot of the peak width (fwhm) as a function of the perpendicular component of the 6D wave vector.

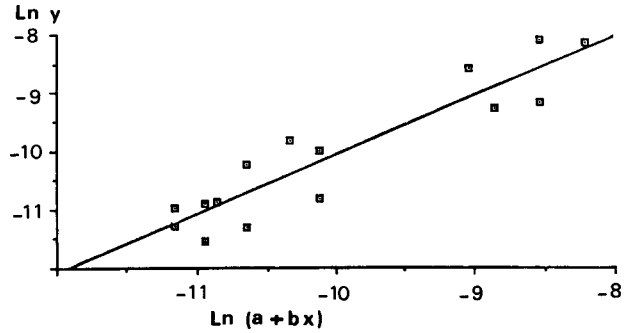

Fig. 5. — Frozen-in phason strain model : $y = (\text{fwhm}/q_\parallel)^2$, $x = (q_\perp/q_\parallel)^2$, $a = 1.36 \times 10^{-5}$, $b = 0.0033$.

There is a wide scatter from the straight line predicted by the icosahedral glass model. A much better fit is obtained if a dependence on both the parallel and the perpendicular components of the 6D-wave vector is considered. The least-square fit of the quadratic law :

$$\omega_\parallel^2 = aq_\parallel^2 + bq_\perp^2$$

leads to $a = 1.36 \times 10^{-5}$ and $b = 3.3 \times 10^{-3}$. These values are of the same order of magnitude as those found for as-quenched i-AlMnSi [10] except that the relative importance of the parallel contribution is here four times smaller than in the case of AlMnSi. That explains the difficulty to put it into evidence : in fact the difference between the agreement ratios of the fits corresponding to the two models results essentially from a few reflections with very small values for $q_\perp$ and large values for $q_\parallel$.

Table II. — *Intrinsic peak widths for the icosahedral phase in a* $Al_{65}Cu_{20}Fe_{15}$ *sample annealed for* 30 min *at* 1 073 K (*instrument resolution* $\Delta q = 3 \times 10^{-4}$ Å^{-1}).

Reflection	$\omega_\parallel$ ($\times 10^3$, Å^{-1})
(7, 11)	0.357
(18, 29)	0.370
(20, 32)	0.358
(52, 84)	0.368

An annealing at 1 073 K for 30 min leads to a striking sharpening of the peaks (see Fig. 2). The intrinsic peak width reduces by a factor of 10 as seen in table II showing the values obtained from those single peaks for which there is no superimposition with reflections from Al_3Fe. After this short annealing treatment, the « high resolution » X-ray measurements show that a small peak broadening still survives, which corresponds to coherently reflecting regions the size of which is roughly $1/\omega_\parallel \sim 2\,800$ Å. The intrinsic peak width is now independent of both $q_\parallel$ and $q_\perp$. It is also independent of the nature of the peaks : both odd indices peaks — corresponding to superstructure reflections — and even indices peak — corresponding to fundamental reflections — lead to the same coherence length : the antiphase domains have essentially the same size as the mosaic grains.

3. CHEMICAL LONG RANGE ORDER IN THE ICOSAHEDRAL $Al_{65}Cu_{20}Fe_{15}$ PHASE. — The structure of the icosahedral *F*-AlCuFe phase can be described as a chemical ordering $P(\mathbf{A}) \rightarrow F(2\,\mathbf{A})$, with two superlattices displaced by half an unit vector of the *F*-cell in 6-D. The presence of smooth antiphase boundaries together with the relative low intensities of the superstructure spots are good indications that the two superlattices are decorated by very similar atomic surfaces with alternating chemical species. The intensities of the superlattice peaks depend on the contrast between these atomic species. A crude estimate of which kind of atoms orders can be obtained by using X-ray anomalous scattering phenomenon : the variation of the scattering factor with wavelength near the absorption edges of the constituent elements produces a variation of contrast in the intensity that is directly related to the nature of the elements.

Assuming in the simplest case that the atomic surfaces at the two sublattices have the same geometry and differ only by the atomic species, we can write the global form factor $F(\mathbf{K})$ in 6D as :

$$F(\mathbf{K}) = (f_\alpha + f_\beta \exp(2\,i\pi\mathbf{K}\cdot\mathbf{T}))\,G_{\alpha\beta}(K_\perp) + f_0(1 + \exp(2\,i\pi\mathbf{K}\cdot\mathbf{T}))\,G_0(K_\perp)$$

where f_α and f_β are the form factors of the atomic species that order between the α and β sublattices with the associated geometric factor $G_{\alpha\beta}(K_\perp)$ supposed to be the same for both sublattices, f_0 and $G_0(K_\perp)$ designates all the orbits that are common to both sublattices, $\mathbf{T}$ is the 6D primitive translation that relates the two sublattices ($T = [1, 0,0,0,0,0]$). Superstructure reflections correspond to half integer values of the phase factor $\mathbf{K}\cdot\mathbf{T}$ whereas fundamental spots correspond to integer values of this phase factor. The ratio of the integrated intensities $\frac{I_s}{I_f}$ of a superstructure *versus* a fundamental reflection is therefore proportional to

$$\frac{I_s}{I_f} \propto \left(\frac{(f_\alpha - f_\beta)\,G_{\alpha\beta}}{(f_\alpha + f_\beta)\,G_{\alpha\beta} + 2\,f_0\,G_0} \right)^2 .$$

Assuming $f_0\,G_0$ to be much larger that the ordering terms and approximately independent on the wavelength, we finally obtain an intensity ratio that varies like $(f_\alpha - f_\beta)^2$ with varying the wavelength. Measurements of the (7-11) superlattice peak and of the (20-32) fundamental peak have been made at four different wavelengths near the absorption edges of Fe and Cu. They lead to the ratios given in table III. A long range chemical ordering between Fe and Cu can be ruled out because the experimental intensity ratio does not vanish near the Cu absorption edge ($\lambda = 1.3923$, second raw in Tab. III). The best linear trend is obtained by choosing as one of the ordering species a random mixture of Cu and Fe in the nominal composition and Al as the other (see last column in Tab. III). These preliminary results suggest that the long range chemical order occurs between an Al orbit and one or several orbits where Fe and Cu are distributed in the proportion of the nominal concentrations. No additional information can be extracted from these sole results concerning a possible short range order between the Cu and Fe atoms.

4. THE SINGLE-PHASE ICOSAHEDRAL ALLOY. — The AlCuFe ternary phase diagram was extensively studied by Bradley and Goldschmidt [18]. A systematic investigation, around the compositions corresponding to the three ternary phases called ψ, ω, and ϕ in their original paper, led us to the conclusion that the ψ phase is indeed the icosahedral phase discovered by Tsai *et al.* [4] in the AlCuFe system. This phase has a small single-phase domain, around the composition $Al_{65.5}Cu_{22.5}Fe_{12}$. However, Bradley and Goldschmidt mentioned that this phase is

Table III. — *Ratio of the integrated intensity of the* (7-11) *superlattice reflection to that of the fundamental reflection* (20-32), *and contrast between the constituent elements, at* $\sin\theta/\lambda = 0.15$, *for different wavelengths.* (f_i : *atomic scattering factor corrected for the anomalous dispersion effect;* $f_{Cu,Fe} = 0.57\ f_{Cu} + 0.43\ f_{Fe}$).

λ	ρ = (7-11)/(20-32) $\times 10^3$	$\lvert f_{Cu}-f_{Fe}\rvert^2$	$\lvert f_{Fe}-f_{Al}\rvert^2$	$\lvert f_{Cu}-f_{Al}\rvert^2$	$\lvert f_{Cu,Fe}-f_{Al}\rvert^2$
1.3839	87	8	128	85	101
1.3923	95	5	128	114	119
1.7482	84	61	33	184	105
1.7902	110	31	65	186	127

difficult to obtain in a pure state and in true equilibrium : they did not succeed in obtaining a single-phase ψ alloy which would give sharp X-ray peaks.

Trying to reproduce Bradley and Goldschmid's results, we had to slightly displace the boundaries of the single phase domain of ψ by a 2.5 % increase in Cu content and a 2.5 % decrease in Al content. During the solidification of the master alloy, we observed a tremendous macrosegregation which can be responsible for large compositional inhomogeneity in the final ingot.

The safest way we found to avoid this compositional inhomogeneity was to produce the master alloy by rapid quenching from the liquid. By this way we have succeeded in preparing, in a perfectly reproducible manner, a single-phase icosahedral alloy which gives sharp X-ray lines. The composition is $Al_{63}Cu_{25}Fe_{12}$; the rapidly quenched alloy is similar to the $Al_{65}Cu_{20}Fe_{15}$ alloy quenched in the same conditions : an icosahedral phase with a small amount of a cubic FeAl-type phase (referred to as β_2 in Bradley and Goldschmidt's paper). After annealing for a few hours at 1 093 K, a single-phase icosahedral structure is obtained (Fig. 6). The high resolution X-ray powder diffraction shows that the peaks have intrinsic widths comparable to those observed for the best standard crystalline powders, and that the peak positions are identical with those calculated for the ideal icosahedral quasicrystal, within the instrumental error.

Subsequent annealing between 1 133 and 1 143 K, during several days, leads to a morphology where relatively large single quasicrystals — the size of which may vary from a few hundreds of microns to several millimeters — generally located at the bottom of the crucible, are surrounded by a cloud of fine quasicrystals (see Fig. 7a) indicating that the growth process developed in a partially melt alloy by coarsening of the icosahedral grains in the liquid. The small grains are almost perfect regular dodecahedra with edges truncated by 2-fold planes and vertices truncated by 3-fold planes. Close examination of small grains show an equivalent morphology for all the vertices, and not only for those related by a single three-fold axis (Fig. 7b), in agreement with the icosahedral symmetry.

Discussion.

The annealed AlCuFe icosahedral phase is a stable phase which gives sharp diffraction peaks located exactly at the icosahedral theoretical positions. Very similar results have also been observed in icosahedral AlCuRu [19].

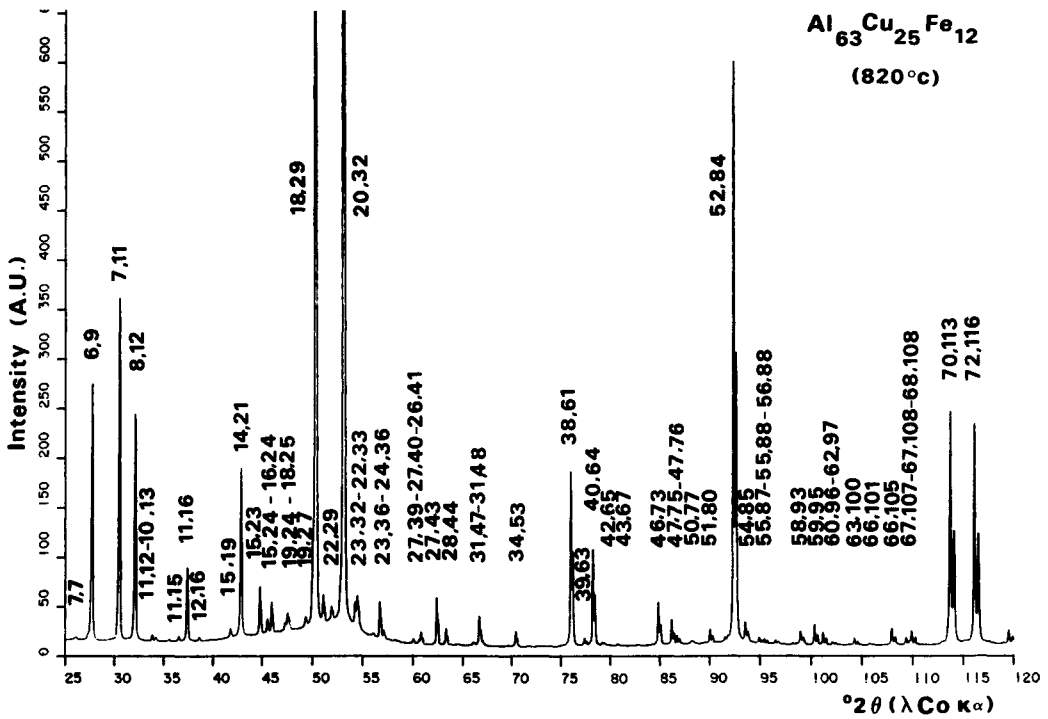

Fig. 6. — X-ray powder diffraction pattern of the single-phase $Al_{63}Cu_{25}Fe_{12}$ icosahedral alloy. The alloy has been quenched by planar flow casting, then the flakes have been annealed for 2 h at 1 093 K.

a) b)

Fig. 7. — (a) Scanning electron micrograph of the single-phase $Al_{63}Cu_{25}Fe_{12}$ alloy initially rapidly quenched and then annealed for 4 days at 1 143 K, showing a large single quasicrystal surrounded by small dodecahedral quasicrystals. (b) Same alloy after annealing at 1 173 K for 15 hours showing a single quasicrystal of about one hundred of microns in size.

Table IV. — *Location of the main diffraction peaks for the icosahedral and the approximant rhombohedral phases ($p = 3$, $q = 2$). Each icosahedral orbit splits into several rhombohedral inequivalent orbits. Although the differences are relatively small, the two phases can be separated by powder diffraction.*

N	M	$Q_\perp$ (Å^{-1})	$Q_\parallel$ ico. (Å^{-1})	$Q_\parallel$ rhomb. (Å^{-1})	δQ (rhomb.-ico.) ($\times 10^3$, Å^{-1})
6	9	0.06297	0.26673	0.26468	– 2.043
6	9	0.06297	0.26673	0.26590	– 0.828
6	9	0.06297	0.26673	0.26795	1.221
7	11	0.04274	0.29292	0.29055	– 2.367
7	11	0.04274	0.29292	0.29530	2.382
8	12	0.07271	0.30799	0.30143	– 6.556
8	12	0.07271	0.30799	0.30881	0.820
8	12	0.07271	0.30799	0.31049	2.504
8	12	0.07271	0.30799	0.31054	2.555
11	16	0.10034	0.35725	0.34965	– 7.605
11	16	0.10034	0.35725	0.35365	– 3.605
11	16	0.10034	0.35725	0.35607	– 1.182
11	16	0.10034	0.35725	0.35839	1.136
11	16	0.10034	0.35725	0.35899	1.735
11	16	0.10034	0.35725	0.36380	6.546
14	21	0.09618	0.40743	0.40115	– 6.284
14	21	0.09618	0.40743	0.40195	– 5.481
14	21	0.09618	0.40743	0.40668	– 0.751
14	21	0.09618	0.40743	0.40676	– 0.674
14	21	0.09618	0.40743	0.41354	6.108
14	21	0.09618	0.40743	0.41564	8.205

Table IV (*continued*).

N	M	$Q_\perp$ (Å^{-1})	$Q_\parallel$ ico. (Å^{-1})	$Q_\parallel$ rhomb. (Å^{-1})	δQ (rhomb.-ico.) ($\times 10^3$, Å^{-1})
15	23	0.08434	0.42504	0.41867	– 6.372
15	23	0.08434	0.42504	0.42198	– 3.063
15	23	0.08434	0.42504	0.42397	– 1.068
15	23	0.08434	0.42504	0.42603	0.992
15	23	0.08434	0.42504	0.42650	1.459
15	23	0.08434	0.42504	0.43055	5.516
18	29	0.02641	0.47395	0.47248	– 1.472
18	29	0.02641	0.47395	0.47542	1.475
20	32	0.04494	0.49834	0.49679	– 1.548
20	32	0.04494	0.49834	0.49680	– 1.536
20	32	0.04494	0.49834	0.49787	– 0.467
20	32	0.04494	0.49834	0.50239	4.052
40	64	0.06355	0.70476	0.70013	– 4.631
40	64	0.06355	0.70476	0.70335	– 1.411
40	64	0.06355	0.70476	0.70335	– 1.411
40	64	0.06355	0.70476	0.70485	0.088
40	64	0.06355	0.70476	0.70502	0.263
40	64	0.06355	0.70476	0.70654	1.782
40	64	0.06355	0.70476	0.70655	1.790
52	84	0.02777	0.80633	0.80382	– 2.504
52	84	0.02777	0.80633	0.80663	0.298
52	84	0.02777	0.80633	0.80729	0.957
52	84	0.02777	0.80633	0.80729	0.959

Such sharp diffraction peaks can be issued from two possible kind of structures : the ideal quasicrystal as obtained from the cut and projection of a 6D hypercubic lattice and the so called random tiling models (see for instance Henley [20]). Both models can be viewed as resulting from a 3-D cut and projection of the 6D lattice : if the cut slice is aligned along the parallel space, the structure is idealy quasiperiodic, whereas if it oscillates around the average parallel space then the structure corresponds to a « random tiling ». If all tiling configurations are assumed to be degenerate in energy, then the structure is, quoting Henley [21], a « maximally random tiling ». The oscillations of the cut slice can be locally locked along rational 3D planes which would give rise to a domain structure of periodic approximants of the icosahedral phase.

In a recent publication Audier and Guyot [22] identified a crystalline structure by electron microscopy in an as-cast ingot of AlCuFe. This phase has been identified as rhombohedral with a large unit cell that can be derived from an inflation by a factor of $2\,\tau^3$ of the prolate rhombohedron of the canonical icosahedral tiling. This phase corresponds to a cut by a rational 3D plane spanned by the three vectors $\mathbf{A} = (2p-q, q, q, q, q, -q)$, $B = (q, 2p-q, q, -q, q, q)$ and $C = (q, q, 2p-q, q, -q, q)$ where $p = 3$ and $q = 2$, very close to the icosahedral cut (in the 5-fold 2D plane, its trace is at 3.19° from the icosahedral one). The rhombohedral parameter is $A_r = \sqrt{2}\,A_{6D}(q\tau + p - q)$ (here, $A_r = 3.786$ nm) ([1]). We have calculated the differences in the location of the diffraction peaks between the icosahedral phase and the approximant rhombohedral phase (Tab. IV). Although the differences are relatively weak, the figure 8, where these deviations are

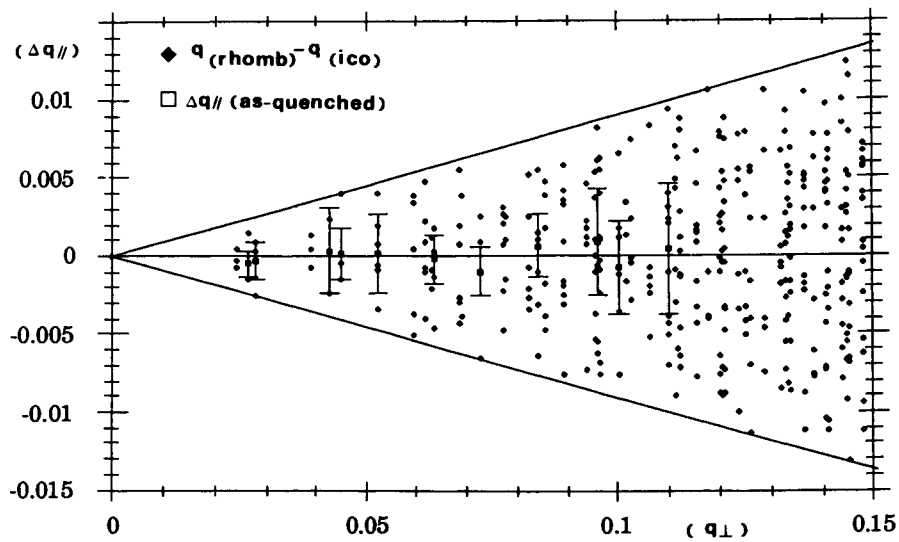

Fig. 8. — Relative position of the diffraction peaks of the 3rd rhombohedral approximant with respect to the ideal icosahedral phase. The bars correspond to the fwhm of the rapidly quenched alloy. They all fit inside the dispersion cone of the rhombohedral phase showing that the rapidly quenched alloy is not a microcrystalline rhombohedral phase.

([1]) A smaller cell can be obtained by the three vectors $A' = \frac{A+B}{2}$, $B' = \frac{B+C}{2}$, $C' = \frac{A+C}{2}$ that corresponds to the parameter $A'_r = A_r \frac{\tau}{\sqrt{\tau+2}} = 3.221$ nm analog to the one found by Audier and Guyot [22].

reported as a function of $Q_\perp$ shows that the two phases can be unambiguously differentiated by powder diffraction. By this way, we confirm that the alloys studied in this paper are really icosahedral phases. On figure 8, the bars are representative of the fwhm of the rapidly quenched alloy ; they are all inside the dispersion cone of the rhombohedral phase, a fact which proves that even these imperfect alloys are not microcrystalline rhombohedral phases.

Deviations from perfect icosahedral symmetry towards periodicity have also been reported in as cast AlCuRu [23] and a major question is to determine which of those phases corresponds to a ground state in the ternary system. In order to check if a crystalline phase would form from the quasicrystalline structure at low temperature, we have performed isothermal annealing at 930 K for 65 hours of the single phased $Al_{63}Cu_{25}Fe_{12}$ sample previously annealed at 1 093 K. We did not observe any changes in the high resolution diffraction patterns nor in the overall morphology of the sample : once formed, the icosahedral phase does not undergo any structural change at low temperatures even after long annealing times.

This apparent discrepancy between Audier and Guyot results and ours seems even to be more flagrant with their additional recent result [24] that the composition of the rhombohedral phase is the same as the one we found for the icosahedral phase (thanks to one of the referees for this information which was unknown to us).

The only difference between their experiments and ours, is the metallurgical process used to produce the phases. Instead of a slow cooling of the ingot, we used an isothermal growth of the single quasicrystals from the liquid. From what is actually observed in computer simulation of growth models, the growth of an ideal quasicrystal is an extremely slow process as compared to crystals and is very sensitive to the surrounding environnement (see for instance Elser [25]). Small anisotropy (composition/temperature gradients, anisotropic stress) during the growth can locally break the icosahedral symmetry. A possible scenario is that, as suggested by the recent results of Hiraga *et al.* in as cast AlCuRu, a linear phason strain develops during the slow solidification, due to local anisotropy that locks the structure along rational hyperplanes leading to a domain structure of periodic approximants. The dodecahedral shapes of the icosahedral quasicrystals indicate that the ternary axes are the « rapid » growth directions. We may therefore expect the anisotropic phason field to develop preferentially along one of the 3-fold axes, which is in agreement with an eventual rhombohedral approximant. This periodic structure, obtained in slowly cooled samples, would therefore be a metastable phase very close to the icosahedral phase with the same composition : a subsequent annealing is needed to eliminate the phason strain for eventually restoring the ideal icosahedral symmetry. Audier and Guyot (and Hiraga *et al.*) results indicate that phason fields are preferentially linear and along rational hyperplanes.

Conclusion.

Two AlCuFe alloys were studied here : $Al_{65}Cu_{20}Fe_{15}$ and $Al_{63}Cu_{25}Fe_{12}$. After quenching by planar flow casting, both alloys have the same structural state : essentially icosahedral, with a few percents of a cubic FeAl-type phase (named β_2 in [18]). However, their state of equilibrium at 1 073 K is different : $Al_{65}Cu_{20}Fe_{15}$ is two-phased, $Al_{63}Cu_{25}Fe_{12}$ is a single-phase icosahedral alloy. This latter is the ideal alloy for the investigation of structure and properties of the icosahedral quasicrystals.

In both alloys, the icosahedral phase may be obtained with no long distance diverging phason disorder : after annealing at 1 073 K, there is no dependence of the diffraction peak width with phason momentum. Hence, this kind of disorder is not an intrinsic character of the icosahedral structure.

The topological disorder in the rapidly solidified icosahedral AlCuFe phase was studied by

X-ray powder diffraction, from measurements of peak positions and peak widths. The peak widths, and the deviations from the theoretical values for the peak positions, are similar to those observed in i-AlMnSi [8, 10]. In both cases, the peak width dependence on the parallel and the perpendicular components of the 6D-wave vector shows that disorder is not purely phasonic : frozen-in phasons are combined with local relaxations of the positions of the atoms. However, this effect appears less strong in AlCuFe than it was in AlMnSi.

A spectacular enhancement of the quasicristalline state towards perfection is obtained by annealing the rapidly solidified AlCuFe alloys. This behavior is quite different from that of the metastable i-AlMnSi phase, for which we did not observe any effect suggesting defect annihilation during heat treatment.

We think that, in order to produce single quasicrystals, it is crucial to grow the material in an isotropic medium at constant temperature by coarsening. This is what is achieved in the process we used to obtain the quasicrystals isothermally from the liquid by a slow coarsening of preexistant icosahedral germs.

The fact that we did not observe any phase transformation from quasicrystal to crystal and that all actually available results unambiguously agree that annealing of as cast or rapidly quenched samples lead to a perfectionning of the icosahedral phase is a strong support to the hypothesis of a true thermal stability of the icosahedral phase which makes it a good candidate as possible groundstate of the ternary AlCuFe system.

The chemical long range order, in the icosahedral phase of the asquenched $Al_{65}Cu_{20}Fe_{15}$ alloy, was studied by X-ray diffraction, taking advantage of the contrast variation between the atomic scattering factors of Cu and Fe near the absorption edges of these elements. We suggest that the chemical long range order results from a substitution of Al by Cu and Fe on primitive orbit(s) in 6D. A Cu/Fe long range ordering is excluded.

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