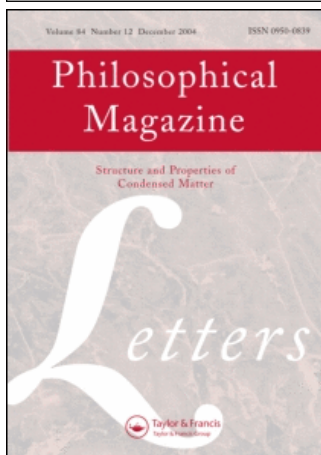


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Transient modulated chemical order during the quasicrystal-to-crystal phase transition of Al-Fe-Cu

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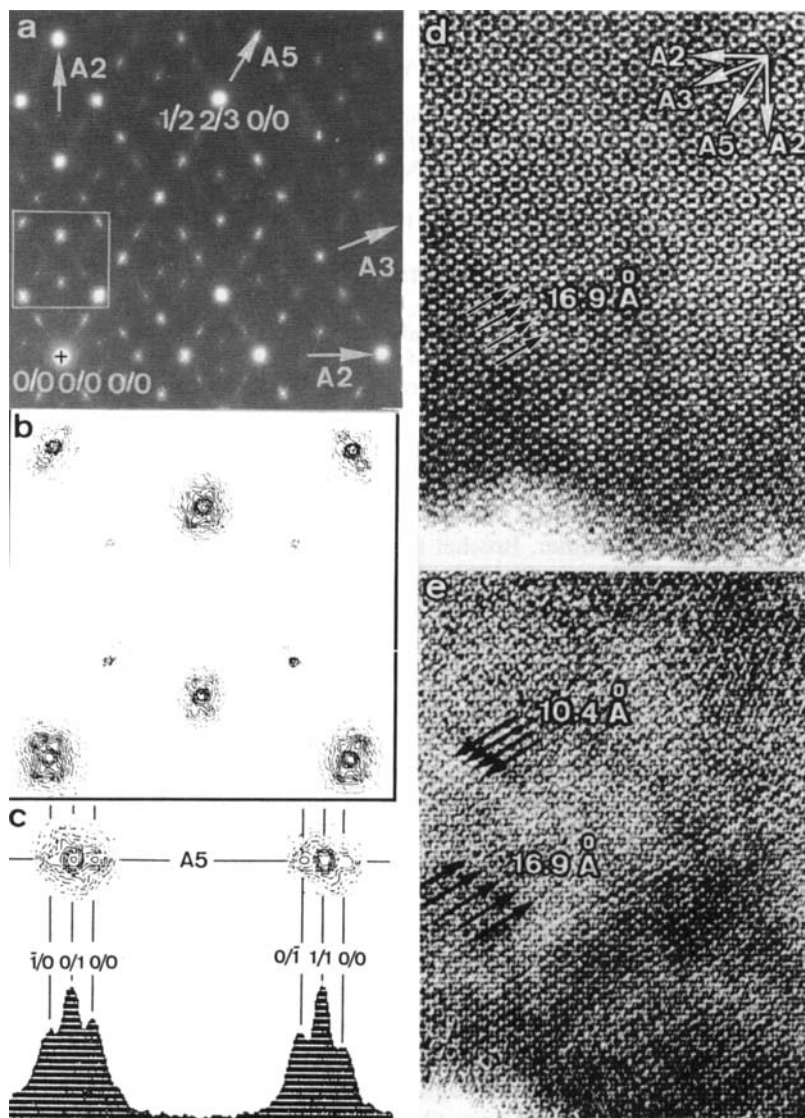
ABSTRACT

A chemical composition modulation, driven by diffusion, is suggested to occur during the transition from the icosahedral to the rhombohedral state of $\text{Al}_{63.5}\text{Fe}_{12.5}\text{Cu}_{24}$, studied as a function of the temperature and time of annealing by electron diffraction, microscopy and X-ray energy-dispersive spectroscopy.

Recently, it has been reported that a reversible rhombohedral-to-icosahedral transition occurs via different transient modulated icosahedral states in an $\text{Al}_{63.5}\text{Fe}_{12.5}\text{Cu}_{24}$ alloy (Audier, Bréchet and Guyot 1990, Janot, Audier, de Boissieu and Dubois 1991, Audier *et al.* 1991). Several structural characteristics of phases involved in this transition have been identified by transmission electron microscopy (TEM); some steps of the transformation have been directly observed by *in-situ* TEM heating experiments and after various annealing treatments of bulk dodecahedral particles (Audier and Guyot 1990a, b). It has been demonstrated that the rhombohedral state is an approximant structure of the icosahedral phase and can be generated by a cut- and-projection method of a six-dimensional F-hypercubic lattice (for example Calvayrac *et al.* (1990)). In relation to six-dimensional approaches and although more experimental work has still to be carried out in order fully to characterize this transition, theoretical works have been attempted for its interpretation. For instance, it has been proposed that this type of transition can be induced by soft-phason modes (Ishii 1990, Janssen 1991); its thermodynamical aspect has been interpreted on the basis of a configurational entropy of random quasi-periodic tiling (Widom 1990). In these studies, it is assumed that the transition occurs without atomic diffusion, that is a transition which could result from 'martensitic' instabilities (Jaric and Mohanty 1987). However, this assumption may not be valid since it has been pointed out in some experimental research that a critical chemical composition could be a characteristic of a very perfect icosahedral phase (Faudot, Quivy, Calvayrac, Gratias and Harmelin 1990, Devaud-Rzepski *et al.* 1989). This means that the origin of a driving force for the transition could imply not only a lattice instability but also a chemical composition variation.

Results, reported in this letter, show that atomic diffusion and chemical composition fluctuations have to be considered in the intermediate states of the rhombohedral-to-icosahedral transition for an alloy of particular composition $\text{Al}_{63.5}\text{Fe}_{12.5}\text{Cu}_{24}$. Such transient modulated states have been observed to form, either by annealing treatments of the as-quenched icosahedral state, in a low-temperature range (about 520-650°C) or by *in-situ* TEM heatings, at high temperatures (between

Fig.1



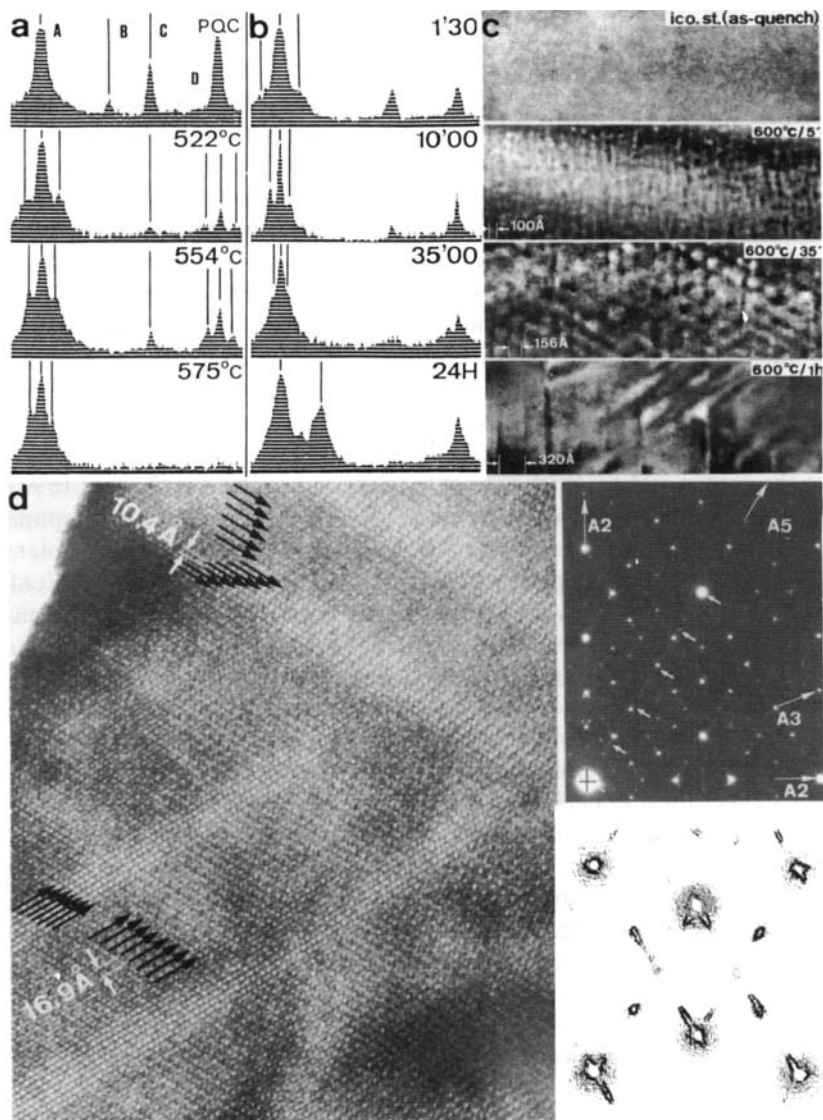
(a) Electron diffraction pattern of twofold zone axis of a modulated icosahedral structure, where the framed part has been analysed in (b) by densitometry from the photo negative (the reflection $1/2\ 2/3\ 0/0$ corresponds to $0.4976\ \text{\AA}^{-1}$). (c) An intensity profile analysis of two reflections along a fivefold direction. (d), (e) High-resolution electron microscopy (HREM) micrographs corresponding to icosahedral and modulated structures respectively (see text).

700 and 750°C). In electron diffraction, the modulation of the icosahedral phase gives rise, around icosahedral reflections, to satellite pairs lying along different fivefold directions (fig. 1(a)). The relative positions of satellites with respect to icosahedral reflections can be accurately analysed by densitometry in an image analysis computer; intensity maxima were determined from iso-intensity level line maps (fig. 1(b)) and from the variation in the intensity along different crystallographic directions, for example a fivefold direction as shown in fig. 1(c). A comparison between high-resolution images of both icosahedral and modulated phases (figs 1(d) and (e)) indicates that slight variations in the contrast result from this modulation somewhat like a tweed pattern when observed at low magnifications (see fig. 3(b)). Viewed at a glance, the high-resolution image (fig. 1(e)) reveals many jags and curvatures in its fringe pattern; such features have been interpreted as resulting respectively from the presence of phason and phonon fields within the icosahedral structure (Socolar 1986, Socolar, Lubensky and Steinhardt 1986). In that case, Fourier transform analyses of high-resolution images may be interesting in order to estimate the relative proportion of phasons and phonons in a modulated icosahedral structure, but with the condition that only phasons and phonons are responsible for the transition. Note that in thin parts of the sample (fig. 1(e)), a few sets of periodic fringes can be observed perpendicular to the fivefold directions; the ratio of the two measured periodic spacings (16.9 to 10.4 Å) is about equal to the golden mean τ . With respect to the rhombohedral cell ($a = 32.16$ Å; $\alpha = 36^\circ$) (shown in fig. 3 of the work by Audier *et al.* (1991)) such distances correspond to the spacings between parallel faces $\{100\}$ of the cell ($d_{100} = 16.91$ Å) and $\{223\}$ planes ($d_{223} = 10.42$ Å), both of which are perpendicular, or nearly perpendicular, to fivefold axes of the icosahedral symmetry group. As previously pointed out, it seems therefore that such a modulated icosahedral state could be characteristic of the beginning of a spreading of periodic order of a rhombohedral type through the icosahedral phase.

From TEM observations on fragments of dodecahedral particles heat treated from an as-quenched icosahedral state and from direct *in-situ* TEM annealing treatments, we have found that the modulation phenomenon evolves continuously as a function of time and temperature annealing. From an analysis of electron diffraction patterns corresponding to different thermal treatment conditions of the material, it can be deduced that the modulation period related to satellite pair distances increases with increasing temperature and time. For instance, such a period varies from about 150 Å at 522°C to 235 Å at 575°C (fig. 2(a)) and from 130 to 380 Å at 610°C as a function of the annealing time (fig. 2(b)). An intensity decrease of the reflections, characteristic of the F-superstructure, is associated with this transformation. However, as pointed out in the following, the structure obtained after 1 h at 600°C and 24 h at 610°C cannot be considered any longer as a modulated state nor as the microcrystalline rhombohedral state.

The modulation of icosahedral states can also be observed in dark-field imaging (fig. 2(c)). Quite a good contrast, resulting from this modulation, can be obtained on images by selecting in dark-field mode a set of intense reflections situated along a fivefold axis. This allows one to measure in direct space an average period of the modulation. In fig. 2(c), the sequence of dark-field micrographs corresponds to a horizontal position of a fivefold axis. The evolution of the modulation is, in that case, observed at constant temperature for different annealing times, the first micrograph being related to the initial as-quenched icosahedral state. Using a video tape recorder, connected to the brightness amplifying camera of the microscope, we have recorded the evolution of the modulation as a function of the temperature when carrying out *in-situ*

Fig. 2



Evolution of the period of modulation as a function of the temperature and time of annealing of the perfect quasicrystal (PQC). A, B, C and D correspond respectively to $0/02/00/0$ (0.06903 \AA^{-1}), $3/24/\bar{1}0/0, 2/\bar{1}1/10/0$ and $\bar{1}/13/00/0$ (0.17994 \AA^{-1}), analysed from diffraction patterns in (a) and (b) and from dark-field micrographs in (c). (d) HREM and electron diffraction patterns (partly analysed by densitometry) of the peculiar structural state obtained after 1 h at 600°C or 24 h at 610°C .

TEM experiments. The results, in agreement with those obtained for thermal treatments of the bulk state, have shown that the average period of modulation seems to increase regularly with the temperature. No discontinuous phenomena have been observed.

As mentioned above, after 1 h at 600°C or 24 h at 610°C, the structure of the material cannot be considered as modulated, because satellite reflections are no longer observed in diffraction; electron diffraction patterns corresponding to this structure (fig. 2(d)) exhibit rows of periodic reflections, which are superimposed on the icosahedral reflections along fivefold directions. The corresponding high-resolution image shows that the periodicity of 10.4 Å, deduced from the diffraction, corresponds to that exhibited in narrow domains or platelets perpendicular to a fivefold direction. Although not visible in diffraction patterns, there are some parts between platelets which can be defined as being periodic and oriented perpendicular to the fivefold directions, with a fringe spacing τ times larger (16.9 Å); this is in agreement with the characteristic distances of the rhombohedral structure previously pointed out in the case of modulated icosahedral structures (fig. 1 e)).

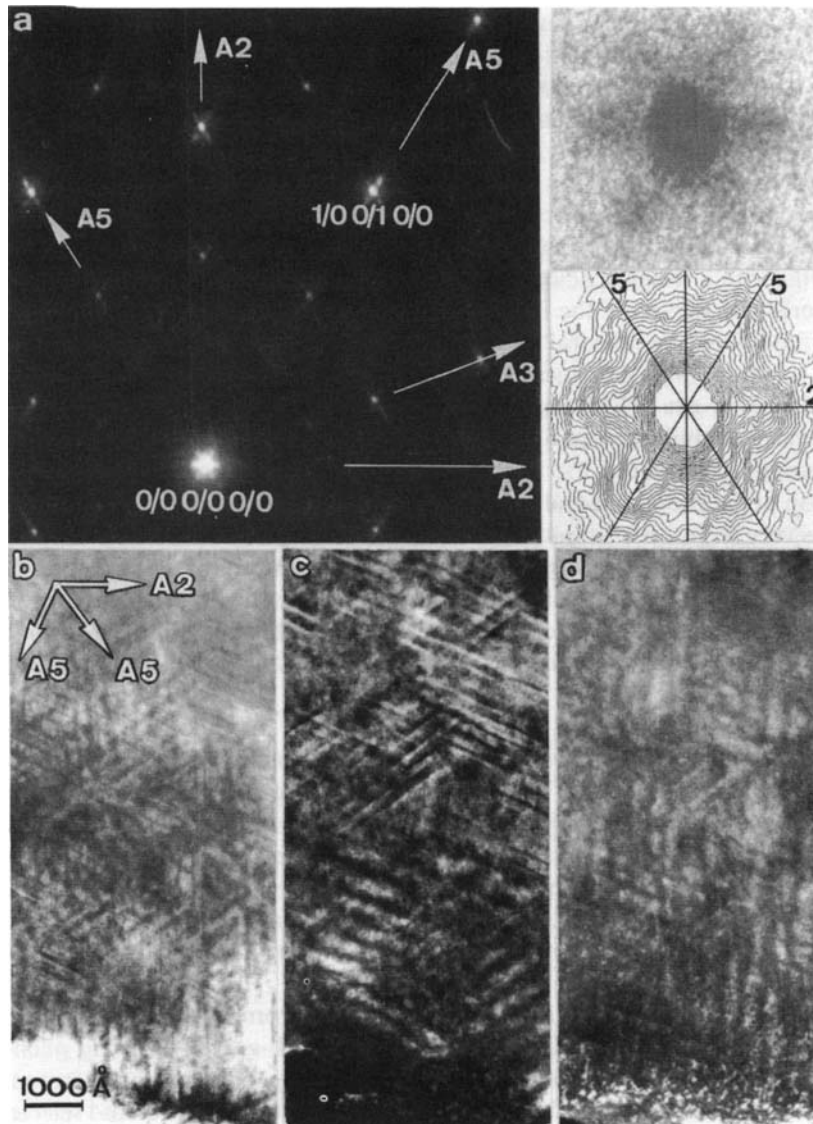
Let us note that the microcrystalline rhombohedral structure has not been recovered by *in-situ* TEM annealing but only after quite long-duration thermal treatments of the bulk state at 675°C. These are experimental conditions which cannot be accurately reproduced for *in-situ* TEM studies. Thus, instead of observing the formation of the rhombohedral structure, the average period of the contrast variation becomes very large, up to about 700–800 Å, after a temperature increase of up to about 700–720°C before disappearing. Electron diffraction patterns of the structure obtained at 700–720°C resemble those of the icosahedral phase but with broader reflections. As previously shown (Audier *et al.* 1991), this state is still not fully typical of a pure icosahedral state, which was only recovered after an *in-situ* thermal treatment at higher temperature.

Finally, we have verified qualitatively that the modulation phenomenon is thermally activated, that is the evolution of the modulation as a function of time is faster at high temperatures. Thus, these results, together with the fact that the modulated states can be easily quenched, indicate that the transition behaviour is rather typical of a phase transition occurring with the help of atomic diffusion.

In relation to this, it was therefore interesting to determine whether or not such a transition occurs with a change of chemical composition. For this, we have carried out two types of experiment: electron small-angle scattering and X-ray energy-dispersive spectroscopy (XEDS).

Electron small-angle scattering has been analysed from conventional selected-area electron diffraction patterns. Good resolution of small-angle scattering phenomena requires only standard adjustments of the condenser lens current of the microscope and of the photographic exposure time. The diameters of both condenser and selected-area apertures are also parameters to be considered. Figure 3 shows an example of satellite reflections observed around the direct transmitted electron beam; satellite reflections are observed along both fivefold directions and along one of both twofold directions. In contrast with X-ray or neutron scattering, electron scattering is dynamic; consequently, small-angle scattering along the direct transmitted electron beam can be due not only to a variation in the specimen electron density but also to multiple diffraction effects. In the present case, the classical construction of the multiple-diffraction effects does not seem to be sufficient for interpreting the different configurations of the satellite reflections observed around the transmitted and close diffracted beams (fig. 3 (a)); that is

Fig. 3



(a) example of small-angle scattered reflections observed on a modulated state ($1/00/1\ 0/0$ is at $0.1117\ \text{\AA}^{-1}$); in the insets are shown an enlarged micrograph of the direct transmitted beam and an iso-intensity level line mapping of it. (b)–(d) bright and dark-field micrographs of a modulated structure from which the relative Bragg and Z contrast effects can be analysed (see text).

satellite reflections lying along fivefold directions are not systematically repeated around each Bragg reflections and those observed along one twofold direction are not repeated at all. The latter reflections are only observed at larger diffraction vectors but result in that case from the curvature of the Ewald sphere. It can be therefore concluded that such small-angle satellite reflections are compatible with a correlated variation in the average electron density, the distance of correlation corresponding, *a priori*, to the modulation wavelength previously measured. Small-angle scattering reflections were not observed in both icosahedral and microcrystalline rhombohedral states but only in modulated icosahedral structures.

The low-magnification bright-field imaging shows a contrast variation which can be interpreted as resulting from at least two effects (fig. 3 (b)): a Bragg and an atomic number Z contrast. Both these contrast effects can be almost distinguished when comparing dark-field images at small (fig. 3 (c)) and large (fig. 3 (d)) scattering angles, that is the contrast depends on both selected Bragg reflections (here reflections have been selected along a fivefold direction) and the relative variation in the squared elastic scattering factors for Cu, Fe and Al, which increases with the scattering angle. Therefore the Z contrast contribution increases with increasing scattering angle. The contrast variation to an electron density modulation perpendicular to the twofold direction along which there is a satellite pair thus becomes visible in dark field (fig. 3 (d)). Such a composition modulation along a twofold direction corresponds in fact to the projected image of that occurring perpendicular to a fivefold direction situated at 58.28° from the twofold zone axis of observation.

XEDS analyses have been first attempted on a scanning transmission electron microscope V.G. HB5 on which an intense electron probe of about 10 \AA diameter can be used. However, these experiments were unsuccessful because of strong beam damage of samples (holes were drilled by the beam during XEDS analyses). The sample stability required the use of a much less intense electron probe. The chemical modulation order has been studied on a JEOL 2000FX scanning transmission electron microscope on a product exhibiting a modulation period of about 150 \AA . In order to achieve a compromise between sufficient statistically reliable values of X-ray intensity (function of the counting time and of the electron probe intensity), limited drift of the specimen and limited contamination, it has been necessary to work out with an electron probe of 200 \AA diameter. This size of probe, larger than the modulation wavelength, cannot allow quantitative measurement of the chemical composition variation but allows one to examine whether it exists or not. Analyses were performed by moving successively the electron probe over steps of distances of about 225 \AA in the direction of a fivefold axis, that is in order to average the intensity over nearly one and two modulation periods. The results shown in the table indicate that there is indeed a statistically

XEDS analyses on a modulated icosahedral structure (the statistical accuracy for each concentration is of the order of 4–5%).

Atomic concentrations, successively measured over nearly one (underlined values) and two modulation periods.								
Al	<u>64.3</u>	62.0	<u>64.1</u>	61.5	<u>64.8</u>	61.9	<u>64.5</u>	62.1
Fe	<u>12.05</u>	13.7	<u>12.1</u>	14.1	<u>11.7</u>	13.9	<u>11.9</u>	14.0
Cu	<u>23.75</u>	24.3	<u>23.8</u>	24.4	<u>23.5</u>	24.2	<u>23.6</u>	23.9

significant chemical variation due principally to change in the Al and Fe atomic concentrations, that of Cu remaining very weak.

As a conclusion, it appears that the transient modulated state involved in the icosahedral-to-rhombohedral transition of $\text{Al}_{63.5}\text{Fe}_{12.5}\text{Cu}_{24}$ is rather complex. An analysis of the HREM images shows that a periodic displacement wave, with phason and phonon components, underlies the transition (Menguy *et al.* 1991). The present results seem to indicate that a chemical composition modulation, driven by diffusion, may also be involved. A relatively large atomic size difference between Al and Fe, Cu atoms (about 13%) is able to correlate the two contributions. Note that from a theoretical point of view, the occurrence of an atomic diffusion and chemical composition change may be possible for a transition described in terms of a linear phason transformations. However, more experimental work and analyses are needed in order to ascertain the role played by phasons and phonons displacements in such a transition.

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