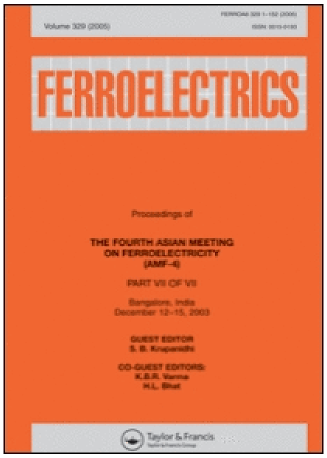

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REVERSIBLE ICOSAHEDRAL-RHOMBOHEDRAL PHASE TRANSITION IN AN $Al_{63.5}Fe_{12.5}Cu_{24}$ ALLOY

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A reversible phase transformation between icosahedral and rhombohedral approximant structures has been studied by T.E.M. The microcrystalline rhombohedral phase, stable at low temperature, transforms into an icosahedral phase via an intermediate pentagonal structure. The icosahedral phase, metastable at low temperature, transforms between 500 and 675°C into the rhombohedral phase via different transient states: modulated icosahedral phases and pentagonal approximants. These intermediate states have been interpreted in the hyper-space description as resulting of shear phason waves, propagating in the perpendicular space. It has to be noticed that chemical composition variations associated to these shear waves and predicted by the theory have been experimentally observed.

Keywords: Quasicrystals, phase transition, modulated states, approximant phases.

INTRODUCTION

Since the discovery in 1984 of an alloy exhibiting diffraction patterns characteristic of the icosahedral symmetry,[1] quasicrystalline structures have been extensively studied. In parallel with important theoretical developments on the comprehension of quasiperiodic structures (i.e. hyper-space crystallography), experimental researches on synthesis and characterization of new quasicrystalline phases have significantly progressed.

One important notion associated to quasicrystalline structures is that of approximant crystalline structures and their transformation into quasicrystals.

The existence of a transition between an icosahedral phase and a rhombohedral approximant has been recently reported in the case of the AlFeCu system.[2,3] Such a transition has been observed by in-situ heating experiments on a transmission electron microscope (TEM) on thin fragments of bulk dodecahedral single crystals.[3] As shown in Figure 1, in the initial state, the electron diffraction pattern exhibits broad and triangularly shaped reflections and the overall symmetry is related to a twofold zone axis of the icosahedral symmetry point group. On the corresponding high resolution electron microscopy (HREM) image, periodic lattice fringes are visible on domains of about 20 nm. After heating by electron beam irradiation, sharp Bragg reflections whose positions are characteristic of a perfect icosahedral phase with a face-centered 6D hypercubic lattice are observed on the diffraction pattern.[4,5] Then, the corresponding HREM image of the same region of the sample exhibits quasiperiodic lattice fringes. The transition is reversible: the microcrys-

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talline state has been recovered after low temperature annealings from the icosahedral phase formed at high temperature.

In the first part of this paper, we shall recall the structural characteristics of the microcrystalline rhombohedral phase. Then, the different transient states of the transition, modulated icosahedral and pentagonal phases, will be described. Their formation are interpreted in the hyperspace description as resulting from the propagation of shearing waves of phason type.

MICROCRYSTALLINE RHOMBOHEDRAL STRUCTURE

Dodecahedral particles with composition $Al_{63.5}Fe_{12.5}Cu_{24}$ have been extracted from the shrink cavities of an ingot cooled from a liquid alloy of initial composition $Al_{63}Fe_{12}Cu_{25}$. As-grown, these crystals exhibits in fact a microcrystalline rhombohedral structure which has been identified from TEM observations. The cell paramèters of the rhombohedral structure are $a_r = 3.216$ nm and $\alpha = 36°$[3,6]; they are closely related to the parameters of the icosahedral structure: the cell is directly related to one of the two Ammann rhombohedra considered in the 3-dimensional quasiperiodic tiling of icosahedral symmetry: the prolate rhombohedra with parameter $a_R = 3.771$ nm and $\alpha = 63.43°$; relations between the two cells are: $\mathbf{a}_r = (\mathbf{a}_R + \mathbf{b}_R)/2$, $\mathbf{b}_r = (\mathbf{b}_R + \mathbf{c}_R)/2$, $\mathbf{c}_r = (\mathbf{c}_R + \mathbf{a}_R)/2$ (Figure 2a). The cell parameter

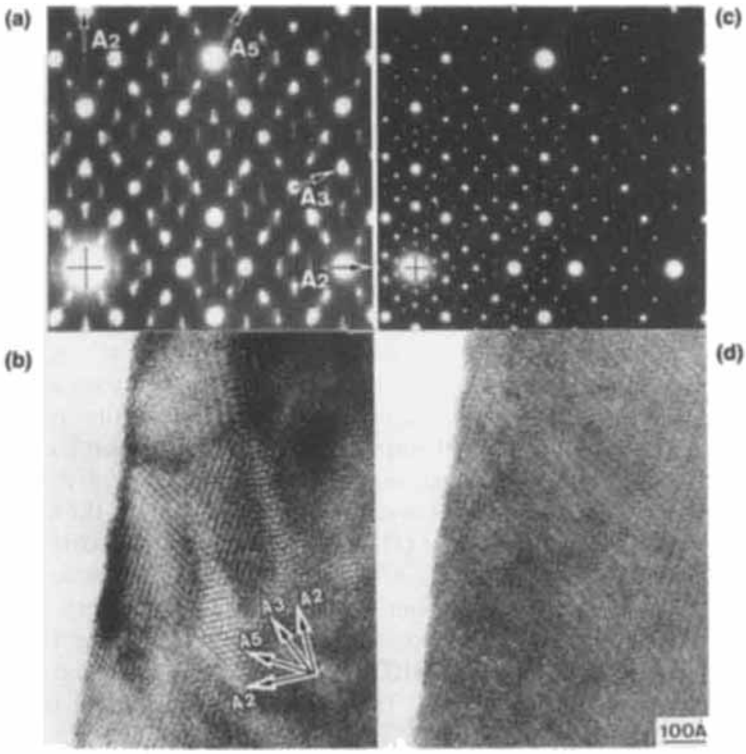

FIGURE 1 SADP and corresponding HREM related to an in-situ transformation experiment between the microcrystalline rhombohedral (a, b) and icosahedral structures (c, d).

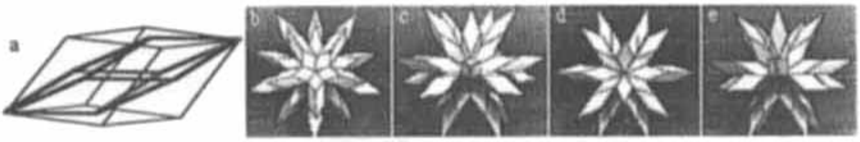

FIGURE 2 (a) Primitive rhombohedral cell (a_r = 3.216 nm, α = 36°) inscribed in the Amann prolate rhombohedron. Stellation constituted of 20 rhombohedra (α = 36°) exhibiting 5-fold (b), 3-fold (c), 2-fold (d) and mirror (e) symmetry elements.

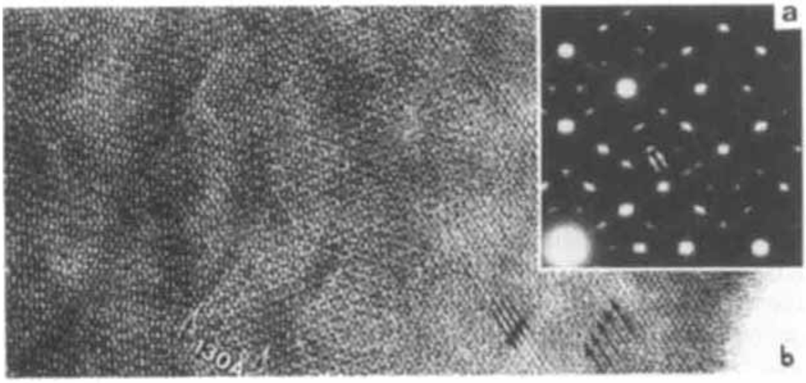

FIGURE 3 (a) 2-fold zone axis electron diffraction pattern related to a modulated icosahedral state and corresponding HREM image (b).

a_R = 3.771 nm is equal to 2 $\times$ τ^3 $\times$ 0.446 nm where 0.446 nm corresponds to the parameter of the perfect icosahedral structure, τ to the golden mean and 2 $\times$ τ^3 to the characteristic inflation of the AlFeCu icosahedral phase of the face-centered hypercubic structure.[7] It has been demonstrated that such a rhombohedral structure is an approximant structure of the icosahedral phase.[8]

The overall pseudo-icosahedral symmetry of the microcrystalline rhombohedral phase results from the peculiar orientational relationships between domains as those existing between the 20 rhombohedra (α = 36°) constituting the stellation of icosahedral symmetry (Figures 2b–e).

TRANSIENT STATES OF THE TRANSITION

The fact that the icosahedral-to-rhombohedral transition may occur via one or several intermediate states has been suggested by an in-situ heating TEM experiment on the quenched icosahedral phase: at about 550°C, a modulation of the icosahedral phase has been observed. The modulation is characterized by satellite spots which appear around each fundamental icosahedral reflection along the 6 fivefold axes (Figure 3a). In that case, the corresponding high-resolution image exhibits a tweed-like contrast with strips perpendicular to fivefold directions (Figure 3b).[9]

Annealing treatments have been performed on bulk dodecahedral particles in order to characterize the different steps of this transition. The results can be summarized as follows:

—the rhombohedral structure is thermodynamically stable at low temperature and results from the transformation of the icosahedral state only stable at high temperature up to melting.[10] The transition icosahedral ↔ rhombohedral occurs at about 675°C in both ways.

—Different transient states appear during this transformation. Concerning the rhombohedral-to-icosahedral transformation, only one intermediate state of pentagonal structure has been observed: its period is equal to 8.453 nm.[11] But several transient states have been observed for the icosahedral-to-rhombohedral transition carried out either by slow cooling from 820°C or by low temperature annealing of the quenched icosahedral phase between 500°C and 675°C. As first phenomenon, satellite reflections lying along the 6 fivefold axes appeared; characteristic of a modulated icosahedral structure, the modulation period increased continuously from about 10 nm to 30 nm with increasing annealing time and temperature. HREM image analyses have revealed that such modulations occur simultaneously along all the 6 fivefold axes. Following is a breaking of the icosahedral symmetry with the appearance of a few periodic fringes perpendicular to the fivefold directions. Further transformations of this modulated icosahedral state depends on the annealing temperature.

Between 600°C and 675°C, it transforms into a mixing of two pentagonal phases. Both have been identified as pentagonal approximants of the icosahedral phase with periodicities equal to 5.225 nm and 8.453 nm,[11,12] the latter being the same as the one observed for the transient state of the rhombohedral-to-icosahedral transformation.

The pentagonal phases transforms finally into the microcrystalline rhombohedral state after a very long time annealing treatment (about 30 days at 600°C). This step in the transformation is not direct: the average thickness and spacing between platelets of the pentagonal approximant of shortest period increase with increasing annealing time but the other pentagonal approximant transforms into a new 3-D quasiperiodic structure which exhibits an important phason-type disorder. The microcrystalline structure appears while platelets of 2nd order pentagonal phase still subsist. The homogenous microcrystalline state has been recovered either by slow cooling from 820°C or after annealing at 675°C for 2 h or annealing at 600°C for 1 month. It has to be noticed that the final texture of the microcrystalline phase does not seem to depend on the thermal history.

Between 500°C and 575°C, the transformation between modulated icosahedral and rhombohedral states seems to occur directly.

Kinetics of the different stages of the transformation are slow and strongly depend on the temperature, indicating that the transformation implies probably atomic

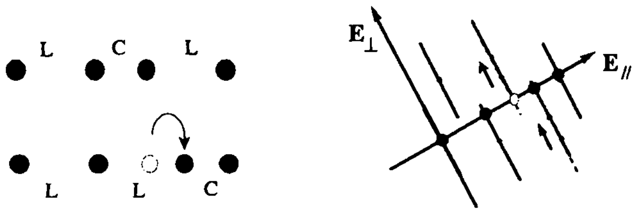

FIGURE 4 (a) Schematic representation of a phason-type atomic jump in an 1-D quasiperiodic sequence and (b) the corresponding description in the 2-D representation.

FIGURE 5 Mechanisms of transformation in the cut and projection method: (a) modulation of the icosahedral phase: sinusoïdal waves of displacement; (b) formation of the two pentagonal phases.

diffusion phenomena. This hypothesis has been confirmed from chemical analyses performed on both modulated icosahedral and pentagonal phases which have revealed that a stoichiometry change can be correlated to structural variations.[13] However, the initial icosahedral and the final rhombohedral states are chemically homogeneous.

MECHANISMS OF THE TRANSIENT STATES FORMATION

From a single crystal X-ray study[14] of the modulated icosahedral phase and a careful analysis of HREM images related to the pentagonal structures, it has been pointed out that the successive transformations may occur via a diffusion phenomenon specific to the quasiperiodic structures: the phason-type atomic jump. For example, the phason transforms a 1-D quasiperiodic sequence of three atoms separated by distances 1 and τ into a new sequence of atoms separated by distances τ and 1 (Figure 4a). In the hyperspace description of the quasiperiodic sequence, this atomic jump in the real space corresponds to a shift of 2 atomic surfaces parallel to the perpendicular space (Figure 4b)[15] (equivalent to the internal space defined in the case of incommensurate structures). This notion of phason can be defined in the same way for 2-D and 3-D quasiperiodic structures.

The formation of the modulated icosahedral state can be considered as resulting from the propagation along the fivefold axes of six displacement waves polarized in the perpendicular space. Each atomic position $\mathbf{x}^0_{6D}$ in the 6-D lattice is modified as follows:

$$\mathbf{x}'_{6D} = \mathbf{x}^0_{6D} + \mathbf{U}_\perp \cdot \cos(\mathbf{Q}_\perp \cdot \mathbf{x}^0_{6D})$$

where $\mathbf{Q}_\perp$ and $\mathbf{U}_\perp$ correspond respectively to the wave vector and the polarization vector of the displacement waves. In the real space, it corresponds to correlated atomic displacements. The formation of pentagonal phases can be interpreted as resulting from a lock-in of the displacement waves: the displacement wave become a saw-tooth shaped function and the slopes of the wave are such that they correspond to the shear generating the 2 pentagonal approximant structures (Figure 5).

CONCLUSION

The different steps of the reversible icosahedral ↔ rhombohedral transition have been studied by TEM and X-ray diffraction. This transition occurs via different transient states: modulated icosahedral and pentagonal phases. The formation of these states has been interpreted as resulting of the propagation of 6 phason waves along the 6 fivefold directions. Finally, concerning the driving force of the transition, it seems that the transformation could result from slight difference with respect to an ideal composition where the icosahedral phase would be stable at all temperature.

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