Ordering Principles in Decagonal Al-Co-Ni Quasicrystals

Walter Steurer*, Antonio Cervellino, Katja Lemster, Stefano Ortelli, and Michael A. Estermann

Abstract: The discovery of quasicrystals has extended the traditional concept that crystalline matter is a periodic arrangement of identical units such as atoms or molecules. The typical quasicrystal is an intermetallic compound in which the building blocks are arranged in a non-periodic but highly ordered way. Of particular interest is the study of these ordering principles as a function of chemical composition and temperature in decagonal quasicrystals where periodic and aperiodic ordering even coexists in the same crystal structure. Structural information from diffraction experiments is the key for revealing these ordering principles and the prerequisite for a comprehensive study of the structure–property relationships. We present here the first all-inclusive *in-situ* high-temperature X-ray diffraction study of decagonal $Al_{70}Co_{12}Ni_{18}$, a stable quasicrystal with a wealth of diffraction phenomena.

Keywords: Al-Co-Ni · Decagonal quasicrystal · High temperature · Order/disorder · X-ray diffraction

'Good order is the foundation of all good things'

Edmund Burke,
Reflections on the Revolution in France, 1790

Introduction

Structural investigations of crystalline materials have contributed much to the present day understanding of the solid state of matter. The foundation to crystal structure analysis with X-rays was laid by Max von Laue at the beginning of the twentieth century by showing that crystalline matter is a periodic arrangement of atoms or molecules, and that an X-ray diffraction pattern of crystalline matter reflects this inherent periodicity. For almost three quarters of a century, crystallinity became a synonym for periodicity and order. This dogmatic belief had to be revised when the quasicrystals were discovered [1]. Quasicrystals exhibit decagonal or even icosahedral diffraction symmetry, which is not consistent with perio-

Correspondence: Prof. Dr. W. Steurer
Laboratory of Crystallography
ETH Zentrum
CH–8092 Zürich
Tel.: +41 1 632 6650
Fax: +41 1 632 1133
E-Mail: steurer@kristall.erdw.ethz.ch
http://www.kristall.ethz.ch/LFK/

dicity, yet the diffraction patterns show sharp Bragg reflections. In fact, the long-range order in quasicrystals can be as good as in perfect silicon crystals.

Technically speaking, the meaning of the term 'crystal' was extended by the *IUCR Commission on Aperiodic Crystals* to 'any solid having an essentially discrete diffraction diagram'. The term 'aperiodic crystal' then means 'any crystal in which three-dimensional lattice periodicity can be considered to be absent.' The structure of aperiodic crystals such as quasicrystals, incommensurately modulated phases and composite crystals, can be properly described as 3D sections of nD hypercrystal structures ($n \geq 3$) (see [2] and references therein). In reciprocal space, this corresponds to a projection of the nD reciprocal space onto the 3D physical space. The number of reciprocal space basis vectors needed for integer indexing the Bragg reflections determines the dimension n of the embedding space.

Many of these quasicrystals are aluminium-based intermetallic compounds, which exhibit technologically important properties such as high strength, corrosion resistance, low thermal conductivity, or high thermopower. The in-depth understanding of the formation and growth as well as the crystal structure of these compounds is a prerequisite when exploring the structure–property rela-

tionships for the design of novel materials.

The activities of the quasicrystal research group at the Laboratory of Crystallography at ETHZ are directed towards the study of the structure of stable decagonal phases, their structural ordering phenomena and phase transformations as a function of composition and temperature. We want to understand the structural building principles of decagonal quasicrystals, the factors governing their formation and stability, as well as the mechanisms of their transformation into differently ordered quasiperiodic phases or periodic crystals. In the following, we present some high-temperature diffraction experiments on decagonal $Al_{70}Co_{12}Ni_{18}$, an example of a quasiperiodic superstructure [3–5].

What is a decagonal phase (Fig. 1)? The structure of a decagonal phase is quasiperiodic in two dimensions and periodic in the third dimension, *i.e.* along the ten-fold axis [2]. Its diffraction symmetry can be described by one of the Laue groups $10/mmm$ or $10/m$, respectively. All reciprocal space vectors $\mathbf{H} \in M^*$ can be represented on a basis $\mathbf{a}_i^* = a_i^*(\cos 2\pi i/5, \sin 2\pi i/5, 0)$, $i = 1,..,4$ and $\mathbf{a}_5^* = a_5^*(0,0,1)$ as

$$\mathbf{H} = \sum_{i=1}^{5} h_i \mathbf{a}_i^*.$$

The vector components refer to a Cartesian coordinate system in physical (parallel) space. Thus, according to the number of independent reciprocal basis vectors needed to index all Bragg reflections with integers, the dimension of the embedding space has to be five. The set of all diffraction vectors **H** forms a Fourier module

$$M^* = \left\{ \mathbf{H}^{\|} = \sum_{i=1}^{5} h_i \mathbf{a}_i^* \Big| h_i \in Z \right\}$$

of rank five in physical space which can be decomposed into two submodules $M^* = M_1^* \oplus M_2^*$. $M_1^* = \{h_1 \mathbf{a}_1^* + h_2 \mathbf{a}_2^* + h_3 \mathbf{a}_3^* + h_4 \mathbf{a}_4^*\}$ corresponds to a Z-module of rank four in a 2D subspace, $M_2^* = \{h_5 \mathbf{a}_5^*\}$ corresponds to a Z-module of rank one in a 1D subspace. Consequently, the first submodule can be considered as a projection from a 4D reciprocal lattice, $M_1^* = \pi^{\|}(\Sigma^*)$, while the second submodule is of the form of a regular 1D reciprocal lattice, $M_2^* = \Lambda^*$. The Bragg reflections related to the Z-module M_1^* fill the reciprocal planes densely. This leads to the fundamental experimental problem of the collection of a 'full data set' [6]. Even a limited section of the physical reciprocal space contains an infinite number of Bragg reflections. Most of them are too weak to be experimentally accessible. To detect all observable reflections the reciprocal space must be mapped employing area detectors.

If decagonal $Al_{70}Co_{12}Ni_{18}$ is described as a superstructure of the nickel-rich basic decagonal phase [3–5] then its reflections can be grouped into three parity classes depending on the value of m

$$m = \left(\sum_{i=1}^{4} h_i \right) \ modulo \ 5.$$

Reflections with $m = 0$ are called main reflections, they are related to the quasiperiodic average structure of the quasiperiodic superstructure. Satellite or superstructure reflections of first order are defined by $m = \pm 1$, those of second order by $m = \pm 2$. Since the main reflections are often given in the setting used for the nickel-rich basic decagonal phase [5], it is useful to give the transformation matrix between both settings

$$\begin{pmatrix} h_1 \\ h_2 \\ h_3 \\ h_4 \\ h_5 \end{pmatrix}_{super} = \begin{pmatrix} 2 & 2 & \bar{1} & \bar{2} & 0 \\ 1 & 4 & 1 & \bar{3} & 0 \\ \bar{1} & 3 & 3 & \bar{1} & 0 \\ \bar{2} & 1 & 2 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} h_1 \\ h_2 \\ h_3 \\ h_4 \\ h_5 \end{pmatrix}_{basic}$$

Fig. 1. Centimetre-sized single crystals of decagonal Al-Co-Ni grown by the self-flux method.

The determinant of the transformation matrix has the value five, *i.e.* the volume of the $5d$ unit cell of the superstructure is five times that of the basic structure (it contains five subcells of the basic structure).

2. Factors Stabilising Quasicrystals

There are two fundamentally different approaches to understand the stability of quasicrystals (see [7] and references therein). The one theory says that an energetically very favourable cluster with non-crystallographic symmetry is the basic building unit of a quasicrystal. The only way to get the maximum packing density of such a cluster in a crystal structure is to pack it quasiperiodically. Since the driving force is the minimisation of energy, the quasicrystal could also be stable at zero K, it could be a ground state of matter. The other theory is based on the special property of quasiperiodic tilings that matching rules are needed for their construction. In absence of these rules, with the only restriction that no overlaps or gaps are allowed, maximally random tilings are obtained. The configurational entropy should be maximum in case of an on average quasiperiodic tiling. At low temperature, nuclei of energetically favourable periodic approximant structures would form and grow larger and larger. The ground state at zero K would be a periodic approximant structure.

There are experimental indications supporting either theory. On the one

hand, most quasicrystals have been found by searching at a given valence electron concentration, *i.e.* assuming a kind of Hume-Rothery-type stabilisation. The electronic conductivity decreases drastically with temperature down to the mK region indicating that the quasicrystal does not undergo any phase transition until that temperature. On the other hand, quasicrystals seem to be best ordered at high temperatures where a significant number of atoms perform phason jumps.

The structural ordering phenomena of quasicrystals as reflected in the variation of the diffraction pattern with temperature (Bragg and diffuse scattering) can give some insight into the stabilisation mechanism of the quasicrystalline phase. If quasicrystals were perfectly quasiperiodic at zero K (*i.e.* energy stabilised) then the number of defects typical for quasiperiodic structures such as atomic jumps related to phason flips of a Penrose tiling (jumps in a double-well potential) should increase with temperature. Within the nD embedding approach, this could be described on a time and space average by a phasonic Debye-Waller factor analogously to the conventional (phononic) Debye-Waller factor. This phasonic Debye-Waller factor strongly depends on the perpendicular space norm of scattering vectors. Consequently, the intensities of reflections with high perpendicular space norm should decrease with increasing temperature.

In case of entropy stabilisation, the ground state was a periodic structure (approximant). With increasing temperature the structure would approach more and more an, on average quasiperiodic, random tiling. The increasing configurational entropy would drive the stabilisation of the quasiperiodic structure. In the nD description the hyperatoms would start to condense with increasing temperature indicating the 'better' quasiperiodic order of the random tiling compared to the approximant. This leads the intensities of reflections with high perpendicular space norm to increase at higher temperature.

We are working, however, on a third, new approach, which – most plausibly – includes both mechanisms of stabilisation, at the same time solving some contradictory or implausible features of both approaches [8]. A basic intermetallic cluster unit would be its base. An ordered, ideally quasiperiodic configuration with this cluster as its basic element would produce a quasicrystal. The ideal quasiperiodicity of the cluster arrangement would be counterbalanced by a strong internal disorder in the component
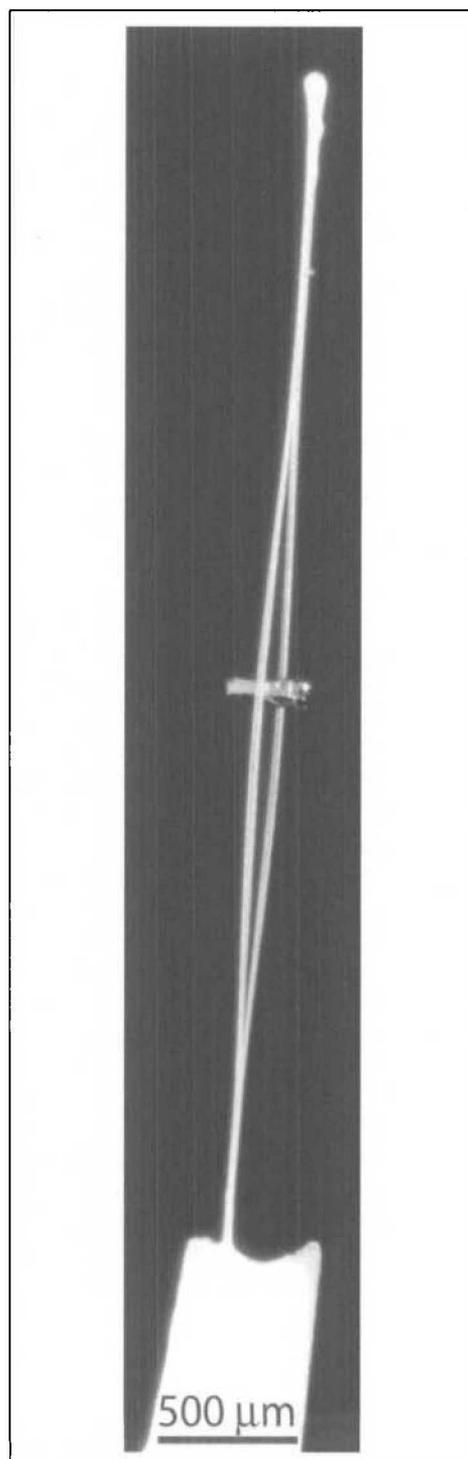
Fig. 2. Single crystal of decagonal Al-Co-Ni clamped between 10 μm-thick alumina fibres. On the upper end, the fibres are glued together with high-temperature cement. At the lower end, they are mounted on an alumina capillary with 500 μm diameter [13].

cluster. Enough entropy (close to the values of metal glasses) can be generated in this way to explain the quasicrystal's thermodynamic stability at high temperature. Long-range-correlation terms in the total energy (explaining and reinforcing the Hume-Rothery effect [8][9]) can be most easily introduced in this way. In this frame, at high temperatures, the ground state would be the quasicrystal, as the structural and energetic limit of approximants with increasingly large unit cell. Small-unit-cell approximants, with more ordered clusters, would be the ground state at lower temperatures. The high-temperature behaviour of the main Bragg reflections can also be easily justified [10], without the need to introduce random tilings in the strict sense, which have never been proven to have Bragg peaks in their diffraction pattern.

3. Diffraction Phenomena at High Temperature

To study the variation of the diffraction patterns with temperature, diffraction data was collected at the Swiss-Norwegian Beam Lines (SNBL) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. For the high-temperature studies we designed and manufactured a furnace with a novel ceramic heating core using a technology known as 'direct ceramic machining' which was initially developed for the fabrication of all-ceramic dental bridges [11][12]. The furnace is designed for the X-ray rotation method and the *mar345* imaging-plate detector system (X-ray Research GmbH). Special emphasis was given to easy handling and good reliability, which is absolutely essential when working within a tight time regime, as for instance at a synchrotron radiation source. We also employed a new mounting technique by clamping the single-crystal specimen between 10 μm alumina fibres instead of gluing it with high-temperature cement onto a holder (Fig. 2) [13].

In the following we show the diffraction data from a single crystal of decagonal $Al_{70}Co_{12}Ni_{18}$. Due to the way the X-ray diffraction data is recorded – with the rotation method at a fixed wavelength – the raw diffraction patterns show a distorted image of the diffraction space (reciprocal space). For further analysis, the raw data has to be processed first into undistorted images of the reciprocal space in a fully quantitative manner. This process involves the interpolation and averaging on a curvilinear grid, and the application of correction factors for specimen absorption, polarisation, and intensity variations of the primary beam. For a typical data set (several hundred frames comprising gigabytes of information) it is not possible to keep the entire data in the main memory of a standard computer. Input/Output (I/O) communication between fast main memory and slower external-memory (hard disk) becomes a major bottleneck. Based on an external memory algorithm, software was developed to handle this challenge (program Xcavate) [14][15]. The reciprocal space section shown in Figs. 3 and 4 were reconstructed from 360 frames with oscillation angle $\Delta\phi = 0.5°$. The sections shown in the first column have been taken at room temperature. The crystal is taken from a sample quenched from 900 °C by switching off the high-vacuum furnace. The sections shown in the second and third column have been taken from the same crystal but now *in situ* at 800 °C and 850 °C, respectively. Going from top to bottom, we see that only every other layer ('Bragg layers') contains sharp Bragg reflections. This sequence of Bragg layers corresponds to a period of two quasi-periodic atomic layers along the tenfold axis. The diffuse interlayers indicate a two-fold superstructure with long correlation length along the ten-fold axis and a much shorter one within the quasiperiodic layers. The correlation length changes, however, with temperature. Going from room temperature to 800 °C, surprisingly, the extended diffuse scattering phenomena condense into almost Bragg reflection-like diffuse maxima. This means, the correlation length of some ordering phenomena increases drastically with temperature while Bragg reflection widths do not change within the experimental resolution. How can this phenomenon be interpreted? We know from many experimental studies that decagonal Al-Co-Ni phases are build from columnar clusters with approximately 20 Å diameter [5]. According to the small width of the diffraction phenomena parallel to the periodic direction, these columns must have rather perfect four-layer periodicity along the ten-fold axis. The narrow width of the Bragg reflections indicates also almost perfect quasiperiodic long-range order of the columns on a two-layer scale. On the four-layer scale, the correlation length is of the order of a few cluster diameters for the quenched sample at room temperature. It increases by one or two orders of magnitude at 800 °C and breaks down almost completely at 850 °C. At this temperature also the four-layer correlation length along the ten-fold axis decreases. This indicates, that at least for this composition, the decagonal phase is better ordered at high temperature.

A closer inspection of the Bragg layers (Figs. 3 and 4) shows that with increasing temperature the intensities of first order superstructure reflections
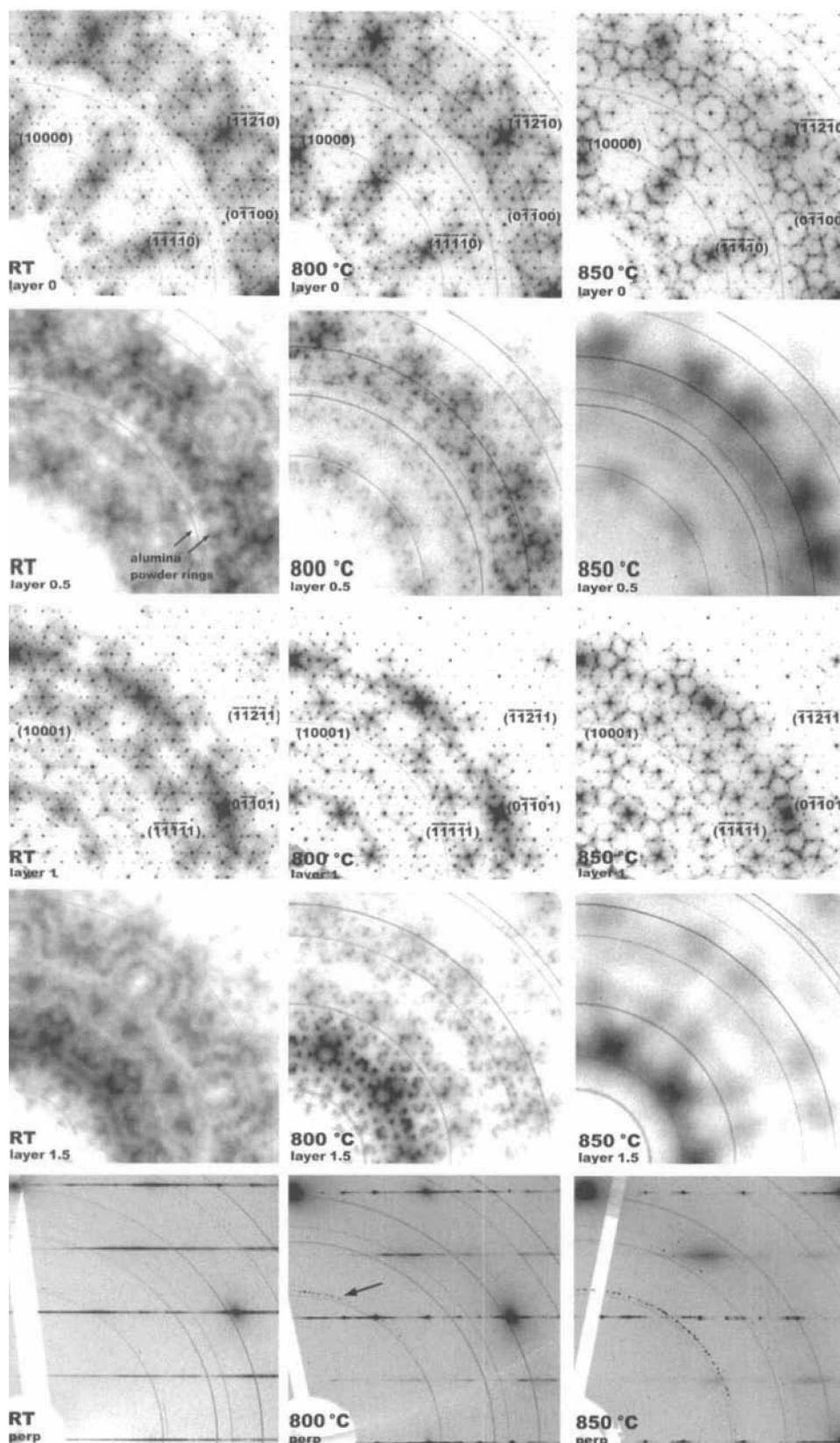
Fig. 3. Series of reciprocal space sections reconstructed from 360 image plate scanner frames at each temperature (*marresearch* 345, wave length $\lambda = 0.7$ Å, oscillation angle $\Delta\phi = 0.5°$, Swiss-Norwegian Beam Lines/ESRF, Grenoble). In the first column, sections of the reciprocal space layers $h_1h_2h_3h_4h_5$ with $h_5 = 0$, 1/2, 1, 1.5 and of the section $h_1h_2\bar{h}_2\bar{h}_1h_5$ perpendicular to them, all taken at room temperature, are shown. The second and the third column contain the sections collected at 800 °C and 850 °C, respectively. The reference basis of Steurer *et al.* [5] was used for indexing.

clearly decrease while those of second order superstructure reflections increase. It is also remarkable that at the same time main reflections with large perpendicular space component of the diffraction vectors strongly increase their intensities. The increase of the intensities of the second order superstructure reflections might also be due to the large perpendicular space components of their diffraction vectors. In previous *in situ* studies, going with exploratory scans close to the melting temperature [16], as well as in investigations on annealed samples [17], it was found that above approximately 940 °C both types of superstructure reflections completely disappeared indicating a second order transition to the basic decagonal phase.

4. Ordering of Clusters

During the last ten years, many structure models have been derived for the basic decagonal phase based on electron microscopic and diffraction studies, for a review see [8]. No quantitative analysis of the quasiperiodic superstructure, however, has been performed yet. Several models have been proposed based on high-resolution electron microscopic studies [18][19] (and references therein). They all have in common that some kind of ordering between the fundamental columnar clusters (≈ 20 Å diameter) is assumed. To get a more quantitative and reliable model, we calculated Patterson and difference Patterson maps using all reflections as well as the different reflection classes separately to figure out the scale and type of ordering phenomena. For that purpose, a large data set (7773 unique reflections) was used that was collected on a sample with nominal composition $Al_{71}Co_{13}Ni_{16}$ with synchrotron radiation at HASYLAB/DESY [4]. The difference Patterson maps (Fig. 5) clearly indicate that the superstructure ordering is on the scale of a Penrose tiling with edge length $a_r = 19.780$ Å [5]. This confirms, that the ordering causing the superstructure reflections occurs between clusters and not within clusters (compare Fig. 5(d)). Since the basic Patterson vectors are strictly oriented at angles $i\pi/10$, $i \in Z$ (compare also Fig. 5(b)), the main inter-cluster ordering must be of the substitutional and not of the displacive type. The strongest peaks of the difference Patterson map calculated from first order satellite reflections indicate a negative correlation between clusters along the long diagonal of the fat Penrose
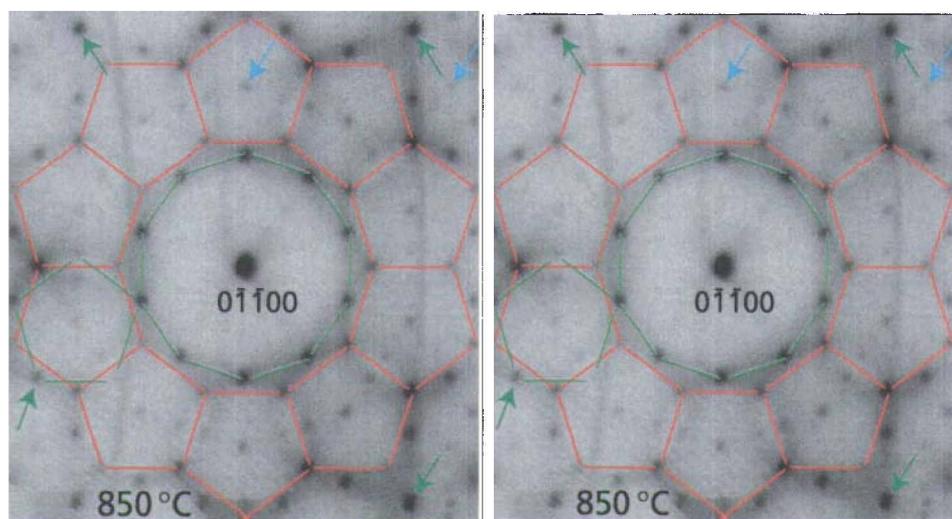
Fig. 4. Enlarged $(h_1h_2h_3h_40)$-sections of the X-ray diffraction data taken at 800 °C and 850 °C, respectively. The surrounding of the $0\bar{1}\bar{1}00$ reflection (i.e. the $3\bar{6}5\bar{1}0$ reflection in the superstructure setting [4]) is shown. Main reflections are guidelined by red pentagons, first order satellite reflections are in the centres of these red pentagons marked by blue arrows and second order satellite reflections by green decagons, pentagons or arrows. The blue star of vectors shows the reciprocal space basis of the superstructure setting, necessary to index all reflections with a quintuplet of integers (fivefold superstructure) [4].

rhomb. In case of maps calculated from second order satellites this is along its edge. This allows the different behaviour of first and second order satellite reflections as a function of temperature to be understood. The satellites (second order) related to the shorter interaction vector of the next neighbours survive to higher temperatures than those (first order) related to the next nearest neighbours along the diagonal of the Penrose rhomb.

5. Conclusions

The present high-temperature X-ray diffraction study of decagonal $Al_{71}Co_{13}Ni_{16}$ gave a first impression and interpretation of the diverse ordering phenomena this phase undergoes with temperature. Future quantitative parametric in situ diffraction studies on a finer temperature scale will give us more insight in the factors governing formation, stability and re-ordering of quasicrystals.

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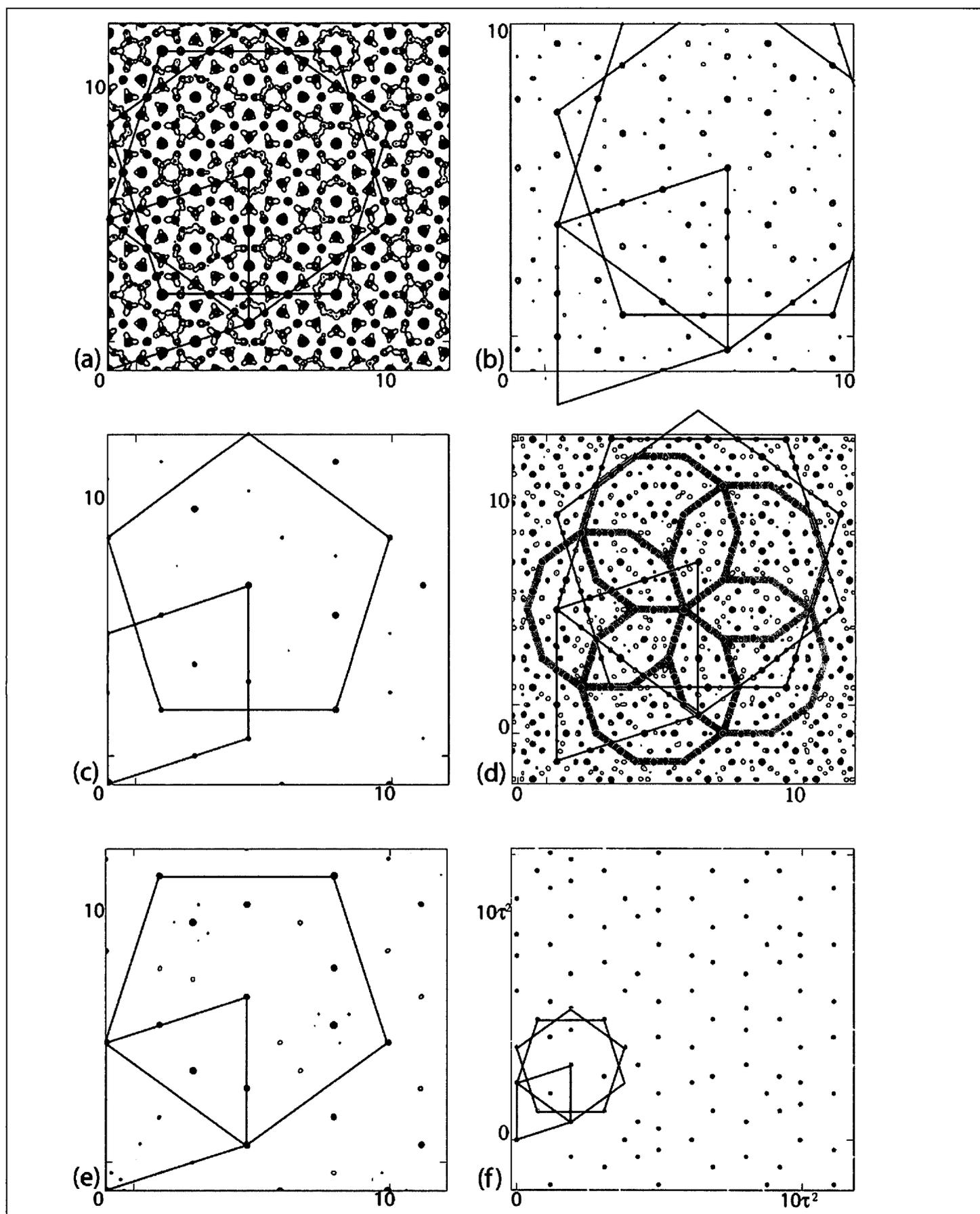[19] K. Hiraga, T. Ohsuna, S. Nishimura, Phil. Mag. Lett. 2000, 80, 653.

Fig. 5. Structural information contained in the superstructure reflections. Patterson maps of the quasiperiodic plane at $x_3 = 0$ are shown calculated from (a) main reflections, (c) first and (e) second order satellite reflections, respectively. Black (red) contour lines indicate positive (negative) values of the Patterson function. Electron density maps of (b) one quasiperiodic plane and (d) of the whole structure projected along the tenfold axis are shown. The rhomb (edge length $a_r = 19.795$ Å) and pentagon vertices mark typical cluster-cluster distances. All units are given as multiples of $a = 3.780$ Å. The cluster centre distribution is shown in (f). Centres of clusters of the parity class p = 1 and with distances of length a_r are connected by lines. The parity classes are related to the position of the respective subcell in the 5D supercell. Subcell numbers n are colour coded: black $n = 0$, $p = 0$; red $n = 1$, $p = 1$, blue $n = 2$, $p = 2$; azure $n = 3$, $p = 2$; pink $n = 4$, $p = 1$.