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An examination of a multiple-twinned periodic approximant of the decagonal phase $Al_{70}Co_{15}Ni_{15}$

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Abstract. High-resolution x-ray scattering was performed on a decaprismatic sample of the nominal composition $Al_{70}Co_{15}Ni_{15}$. The overall diffraction pattern has tenfold symmetry within experimental resolution, but many low-indexed reflections reveal a splitting, which is evidence for twinned high-order periodic approximants of the decagonal phase, rather than for a truly decagonal quasicrystal. To our knowledge, we report the clearest separation of this kind of splitting to date. For the orthorhombic approximant, the space group *Cmm* with lattice parameters $a = 61.024(5)$ Å, $b = 83.99(1)$ Å and $c = 4.0799(5)$ Å was derived. Deviations from the diffraction pattern predicted by the twinning model were observed. We point out the close similarity between the x-ray diffraction of the real decagonal quasicrystal and that of our twinned sample.

1. Introduction

Decagonal quasicrystals are characterized by their unique tenfold symmetry axis. While the arrangement of the atoms is quasiperiodic in planes perpendicular to the tenfold axis, decagonal quasicrystals exhibit translational symmetry parallel to the tenfold axis. So they represent an intermediate state between icosahedral quasicrystals and ordinary crystals with anisotropic structural properties. Periodic approximants of the decagonal quasicrystal are an intermediate state between decagonal quasicrystals and ordinary crystals: they have approximately tenfold diffraction patterns, but are in fact periodic crystals with large unit cells. Since the approximants of a decagonal quasicrystal occur in the same compositional range as the decagonal quasicrystal, a structural relationship between the two systems must be expected.

In the ternary system Al–Co–Ni, a thermodynamically stable decagonal phase is observed [1]. Its stability range and the occurrence of crystalline phases in the Al–Co–Ni phase diagram near the decagonal area have also been reported by Kek [2]. Song *et al* [3], and independently other authors, recently pointed out the close similarity between diffraction patterns of true decagonal quasicrystals and twinned periodic approximants of similar nominal composition on the isotypical system Al–Cu–Co. The occurrence of periodic approximants of the decagonal phase of Al–Co–Ni has been reported by Edagawa [4]. Those studies are almost entirely based on TEM experiments and additional x-ray powder diffraction, and give only estimated values for the lattice constants. In contrast, for a structure analysis based on x-ray scattering data, comparatively large single crystals are required. They have to be sufficiently well characterized, especially when comparing the

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TEM data of decagonal quasicrystals and approximants [3]. The five-dimensional structure analysis [5, 6] on both systems was based on x-ray diffraction of decagonal single crystals. A characterization of approximant phases by means of single-crystal diffraction is highly desirable, as five-dimensional structure refinement implicitly assumes that the examined sample is in a quasicrystalline rather than in an approximant phase.

A recent study by Fettweis *et al* [7] on Al–Cu–Co–Si exhibits the possibility of distinguishing between true quasicrystals and twinned approximants (or microcrystalline states [8]) in x-ray-scattering experiments. The authors point out that diffraction patterns with spots of low momentum transfers (less than 0.5 $Å^{-1}$) must be examined for characterization purposes. The $Al_{70}Co_{15}Ni_{15}$ system studied here shows similar diffraction phenomena, recorded with even higher resolution with our experimental set-up. In the following, the additional information contained in the high-resolution data is discussed.

2. Twinned periodic approximants of the decagonal phase

Song *et al* [3] reported on multiple split Bragg reflections in TEM experiments on decagonal $Al_{65}Cu_{20}Co_{15}$, and gave a detailed description of the twinning effect: the diffraction pattern usually is modelled in two dimensions by a superposition of five periodic lattices, in the present case with lattice constants of $a = b = 51.91$ Å and $\gamma = 108°$, rotated by 36° with respect to each other. Figure 1 gives a sketch of the superposition. Areas with several Bragg peaks of different domains, rather close to each other, are enlarged at the bottom of figure 1. They reveal a characteristic geometrical formation. Examination of the reciprocal space reveals several remarkable features. Characteristic types of splitting are found mainly on two different axes: type-I and type-II reflections are found alternatingly in ⟨10000⟩ directions of the decagonal quasicrystal, and type III and type IV are on the second twofold axis, $\langle 100\bar{1}0\rangle$, of the decagonal quasicrystal. Here quasicrystal indexing [2, 6] is used for convenience. In the following we will generally use the unit cell for the approximant when indexing reflections, as there is a close relationship in indexing the periodic approximant and the decagonal phase: table 1 gives indices of selected sets of five neighbouring approximant reflections and the corresponding quasicrystal index for [10000]. Both indices of the centre reflections (rotation angle 0°) are always members of the Fibonacci series 1, 2, 3, 5, 8, 13, 21, 34,..., implying that the ratio $|Q_1|/|Q_2|$ of momentum transfer of two consecutive type-I and type-II centre reflections approaches the golden mean $\tau \simeq 1.618\,034$, which is also a characteristic number in quasicrystalline diffraction patterns (as $\lim_{i\to\infty} F_{i+1}/F_i = \tau$, for F_i elements of a Fibonacci series). Furthermore, the other four reflections, also indexed with Fibonacci numbers, are arranged in a way that results in decreasing reciprocal-space distances with increasing momentum transfer. This fact is not mentioned too often, though its consequences are rather stringent: with increasing momentum transfer, the splitting is more difficult to resolve for a given resolution. Moreover, if the splitting remains unresolved, the geometrical centres of two consecutive type-I and type-II reflections are characterized by $|Q_{cI}|/|Q_{cII}| = \tau$. That is the reason why one cannot distinguish between the decagonal quasicrystal and twinned periodic approximants within a given resolution.

Here we summarize the main properties of a truly decagonal quasicrystal with regard to the indexing: the strongest peaks are indexed in the tenfold-symmetry plane with reference to the five vectors, which point towards the edges of a regular pentagon; the Bragg spots then are indexed based on four of them, since the fifth is the sum of the other four. The last index refers to the c-axis. So five indices denote a quasicrystal peak. Related to the geometry of a regular pentagon, the distances of quasicrystal peaks obey the golden mean τ.

Table 1. Type-I and type-II reflections occur on a twofold axis for the twinned system at special positions. Indexing for the five components of consecutive type-I and type-II reflections is given. For comparison the related quasicrystal peaks are listed.

Rotation angle (deg)	Type I	Type II	Type I	Type II	Type I
0°	3, 3	5, 5	8, 8	13, 13	21, 21
36°	5, 0	8, 0	13, 0	21, 0	34, 0
72°	5, $\bar{3}$	8, $\bar{5}$	13, $\bar{8}$	21, $\bar{13}$	34, $\bar{21}$
108°	3, $\bar{5}$	5, $\bar{8}$	8, $\bar{13}$	13, $\bar{21}$	21, $\bar{34}$
144°	0, $\bar{5}$	0, $\bar{8}$	0, $\bar{13}$	0, $\bar{21}$	0, $\bar{34}$
Quasicrystal index	20110	$\bar{1}0\bar{1}\bar{1}0$	10000	$00\bar{1}\bar{1}0$	$10\bar{1}\bar{1}0$

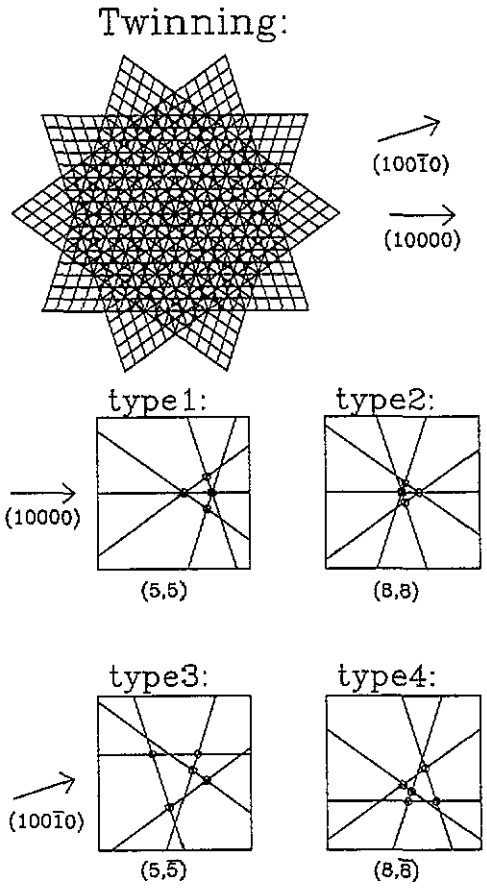

Figure 1. Model of a multiple-twinned periodic approximant of the decagonal phase [7]. Areas with closely lying peaks of different domains are enlarged. They occur on the two twofold-symmetry axes in this system.

As a reference for tenfold diffraction patterns of decagonal quasicrystals see [2], [5] and [6].

3. Experimental details

The experimental data were collected at two different experimental stations. For single-crystal x-ray diffraction with optimum resolution a three-crystal diffraction set-up was used in the laboratory in Kiel: radiation of Cu $K\alpha_1$ wavelength is generated by a 12 kW rotating-anode device. By use of Si(111) single crystals as both monochromator and analyser, the best achievable experimental resolution exceeds 5×10^{-5} Å^{-1} in $Q_\perp$ and 3×10^{-4} Å^{-1} in $Q_{||}$, depending on the absolute value of momentum transfer $Q_{||}$. Here $Q_\perp$ denotes the direction perpendicular to $Q_{||}$ in the measurement plane. As reported in [9], the minimum step width is 5/10000°, and therefore does not limit experimental resolution. Additional experiments were performed with synchrotron radiation at the four-circle diffractometer at HASYLAB/Hamburg (beamline D3). Here we are no longer restricted to one measuring plane by the availability of an Eulerian cradle, and due to the large primary intensity we have the possibility to detect weak reflections. It has to be kept in mind that the best resolution is obtained in the zero reciprocal lattice layer, due to both the anisotropy of the resolution function and the sample orientation. In this study we mostly restrict ourselves to measurements in the tenfold-symmetry plane. Since currently no analyser crystal is provided at D3, resolution is slightly worse than in the laboratory measurements. For standard crystallographic applications, higher resolution is normally not required.

The sample was prepared by slow cooling from the melt down to room temperature, a method which seems to be favourable for the growth of large quasicrystalline single crystals. Edagawa *et al* [4] report a strong tendency towards twinning for such samples, while quenched samples often show diffraction patterns with broader spots and less intensity. An annealed (800 °C) and quenched sample (sample 2) was also mounted and we present the first results at the end of this paper. Five-dimensional structure refinement on a decagonal quasicrystal of the same composition (annealed at 850 °C and quenched) was recently undertaken by Steurer *et al* [6]. The five-dimensional lattice constants were determined to be $a_i = 3.794(1)$ Å, $i = 1, ..., 4$ and $a_5 = 4.0807(3)$ Å, where a_i denotes the lattice constant for the quasicrystalline structure description in the aperiodic plane (a–b plane in the approximant phase) and a_5 is the lattice constant perpendicular to the the tenfold-symmetry plane. The reciprocal lattice constants are $a_i^* = 0.2636(1)$ Å^{-1}, $i = 1, ..., 4$ and $a_5^* = 0.245\,06(3)$ Å^{-1} in crystallographic notation. In the following our aim is to examine the structure of some strong reflections of the related twinned periodic approximant.

4. Results and discussion

First the results of the measurements at the rotating anode will be summarized. They give clear evidence for twinning phenomena: the most intensive spots at low momentum transfer for the quasicrystal indexing are the reflections 10000, $00\bar{1}10$, $10\bar{1}10$ and $100\bar{1}0$. They all are located on the two twofold-symmetry axes. The tenfold symmetry in the measurement plane was verified by comparing the 10000 reflection and its symmetry-related reflections with regard to peak positions.

For the twinned periodic approximant, in the a–b plane a splitting near the theoretical position of the 10000–quasicrystal reflection is well resolved—five spots are visible and a contour plot of the intensity in this environment is shown in figure 2(a). Inspection of the other three Q-space regions shows that at least two of them exhibit more than one single reflection (see figure 2(a), (b)). For the reflection $10\bar{1}10$ the splitting is not resolved, but the measured peak is broader than the resolution function. We conclude that the splitting is present but buried. In all cases the twofold symmetry is perfectly obeyed. In table 2 the

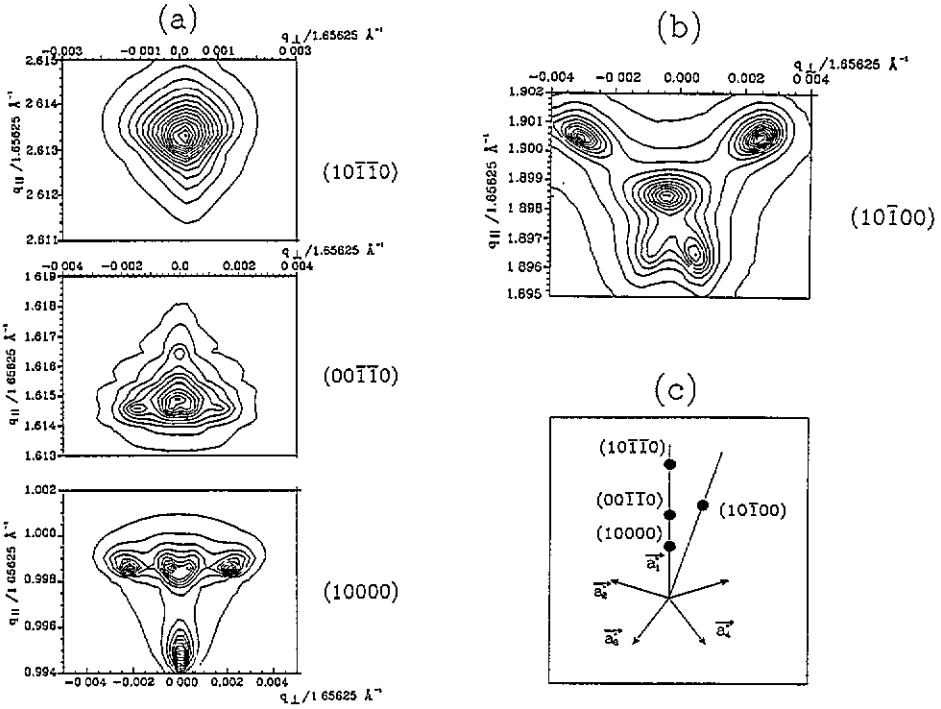

Figure 2. High-resolution x-ray scattering on sample 1, recorded at the rotating anode. The characteristic splitting for twinned periodic approximants is visible. (a) Contour plots of the strongest reflections along the [10000]-direction (these are 10000, 00$\bar{1}\bar{1}$0 and 10$\bar{1}\bar{1}$0 in quasicrystal indexing). (b) Contour plot of the 10$\bar{1}$00 reflection. (c) A description of the examined areas in reciprocal space. The vectors are the basis for quasicrystal indexing in the a–b plane.

peak positions extracted from the data are summarized. The table also gives peak positions for the quasicrystal based on the lattice constants derived by Steurer *et al* [6]. They do not coincide with any of the peak positions exactly, but are quite close.

The full width at half maximum (FWHM) of these peaks agrees with that of the resolution function at the given momentum transfer, indicating extremely large coherence lengths ($\sim$ 5000 Å).

Most remarkable is the occurrence of five rather than four separate reflections for type-I and type-II reflections, since the twinning model for the ideally twinned system ($\gamma = 108.0°$) predicts identical positions of the reflections 13, 0, 0 and 0, $\bar{13}$, 0. For the four investigated areas, the best agreement with the measured peak positions was found for lattice constants $a = b = 51.90$ Å and $\gamma = 107.97°$ instead of $a = b = 51.91$ Å and $\gamma = 108.0°$. To preserve tenfold symmetry, the rotation angle by which two domains are twisted remains a multiple of 36°.

In order to check the preliminary model, Q-scans were performed at the four-circle diffractometer at HASYLAB beamline D3, using a wavelength of 0.71 Å. First, lattice parameters for the approximant were refined from 58 centred reflections in the range $20° \leqslant 2\theta \leqslant 80°$: $a = 51.911(5)$ Å, $b = 51.907(5)$ Å, $c = 4.0799(5)$ Å, $\alpha = 90.00(2)°$, $\beta = 90.00(2)°$ and $\gamma = 108.00(1)°$. Assuming $a = b$, this cell is equivalent to an orthorhombic unit cell that has the following lattice parameters: $a = 61.024(5)$ Å,

Table 2. The peak positions of the most intensive quasicrystal reflections, calculated according to [6], are compared with the measured peak positions.

Quasicrystalline index	$\|Q\|$ (Å^{-1})	Measured $q_{\|\|}$ (Å^{-1})	Peak position $q_\perp$ (Å^{-1})
10000	1.6560(4)	1.6475(5)	±0
		1.6539(5)	−0.0036(2)
		1.6539(5)	−0.0006(2)
		1.6539(5)	0.0006(2)
		1.6539(5)	0.0036(2)
$00\bar{1}\bar{1}0$	2.6795(3)	2.6772(5)	±0
		2.6742(5)	−0.0025(2)
		2.6743(5)	−0.0003(2)
		2.6743(5)	0.0003(2)
		2.6743(5)	0.0025(2)
$10\bar{1}\bar{1}0$	4.3355(7)	4.3281(5)	±0
$100\bar{1}0$	3.1499(8)	3.1444(5)	±0
		3.1410(5)	−0.0008(5)[a]
		3.1410(5)	0.0013(2)
		3.1410(5)	−0.0045(2)
		3.1410(5)	0.0045(2)

[a]This spot has very weak intensity and only appears as a shoulder.

b = 83.99(1) Å, c = 4.0799(5) Å. As worked out in [10] and according to the terminology of Edagawa *et al* [4], the lattice parameters correspond to a (5,7) approximant. The spacegroup for the approximant is probably $Ccmm$, a subgroup of $P10_5/mmc$, the spacegroup for the decagonal phase. Extinction rules were checked for l = 0, 1, 2, 3, ... From a comparison with the TEM results of Song *et al* [3], Edagawa *et al* [4], and the results of Fettweis *et al* [7] we conclude that they all have observed the same phenomenon in the tenfold-symmetry plane (table 3). Below, the indexing follows the primitive (monoclinic) unit cell for the approximant. Instead a five-dimensional indexing can always be used for each Q-space area which reveals splitting.

Table 3. Lattice parameters derived for periodic approximants of decagonal phases.

Reference	Lattice parameters	Nominal composition
Song *et al* [3]	$a = b = 52$ Å and $\gamma = 108°$	$Al_{65}Cu_{20}Co_{15}$
Fettweis *et al* [7]	$a = b = 51.915$ Å and $\gamma = 108°$	$Al_{63}Cu_{17.5}Co_{17.5}Si_2$
Edagawa *et al* [4]	$a = 38$ Å, $b = 52$ Å and $\gamma = 90°$	$Al_{70}Co_{15}Ni_{15}$
	$a = 62$ Å, b: quasiperiodic, $\gamma = 90°$	$Al_{70}Co_{15}Ni_{15}$
This study	$a = 61.024(5)$ Å, $b = 83.99(1)$ Å, $\gamma = 90°$	$Al_{70}Co_{15}Ni_{15}$

In normal ω-scans, the conventional set-up for collecting crystallographic data-sets, the splitting can be guessed but details remain unresolved. In order to enhance resolution, further Q-scan measurements were done with a 0.1 × 4 mm entrance slit. In figure 3 two Q-scans for the 13, 0, 0 reflection (10000 in quasicrystal indexing) in the tenfold-symmetry plane with comparable extension are presented. The top one was recorded with a 4 × 4 mm entrance slit. Here, especially along [h, 0, 0], the resolution is obviously not sufficient to resolve the splitting. For the bottom picture, a decreased detector opening was used and now the splitting is well resolved. As a consequence, one may say that enhanced resolution

is indispensible for reliable measurements.

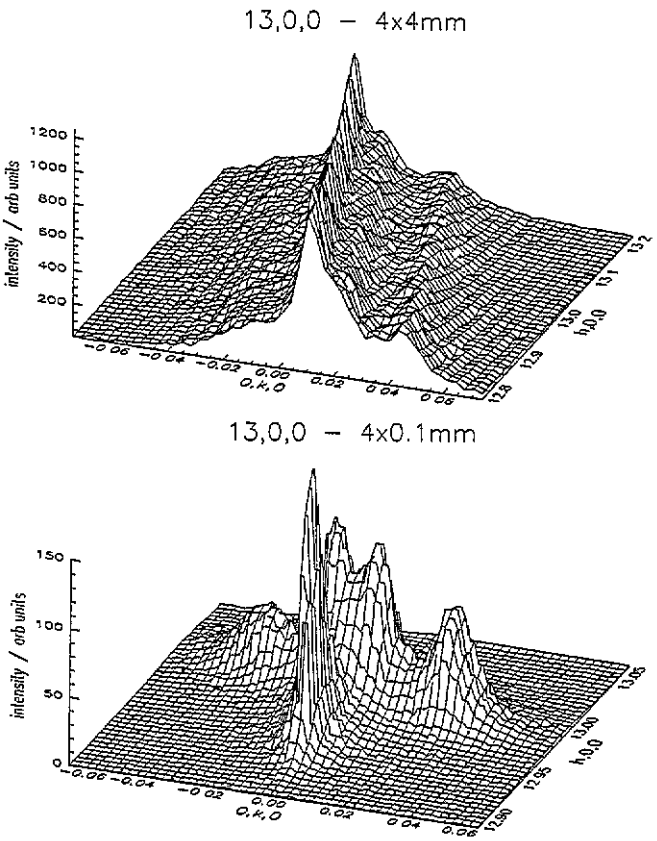

Figure 3. Resolution effect at the four-circle diffractometer D3 (HASYLAB, Doris III): the 10000 quasicrystal reflection, measured with a detector opening of 4 × 4 mm (top) and of 0.1 × 4 mm (bottom). The regions shown have comparable extension. Intensities are given in counts per second.

A high-resolution scan along [1, 1, 0] (figure 4) indicates that periodicity is indeed very well established. The Fibonacci-indexed reflections are strongest, but also the other reflections h, h, 0 show appreciable intensity (not measured and probably not visible at the rotating anode). The reflection 8, 8, 0 has a maximum intensity of 60 000 counts per second. At the rotating anode we measured about 80 counts per second.

As a consequence of the twinning model, the reflections h, 0, 0 of a different domain should be found on the same axis. Here only the Fibonacci-indexed reflections were detected (5, 0, 0, 8, 0, 0 and 13, 0, 0). They nearly coincide with 3, 3, 0, 5, 5, 0 or 8, 8, 0, respectively. We conclude that the direction [1, 0, 0] of one domain is not exactly the same as [1, 1, 0] of another domain. In order to find the correct lattice parameters, Q-space planes in the a–b-plane were recorded around additional reflections. Figure 5 shows the surroundings of 5, 0, 0 and 8, 0, 0 and, for comparison with the laboratory measurements, of 13, 0, 0. Again, as for the laboratory measurements, the ideal lattice parameter $\gamma = 108.00°$ gives incorrect peak positions without further assumptions, especially for h, 0, 0 and 0, $\bar{h}$, 0. These two reflections coincide in the ideal case. On the other hand, a departure of γ from 108.00° does not yield consistent peak positions for

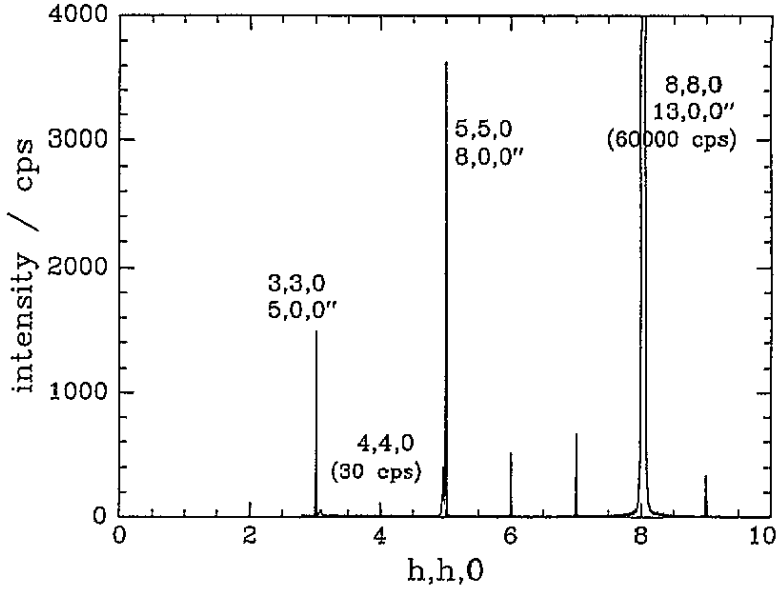

Figure 4. High-resolution scan along the [110]-axis of the periodic approximant, recorded at D3. All reflections h, h, 0 have appreciable intensity. On this axis from the h, 0, 0 reflections of a different domain only 5, 0, 0, 8, 0, 0 and 13, 0, 0 were found.

all surroundings. Otherwise, one should find decreasing distances in reciprocal space for the reflections h, 0, 0 and 0, $\overline{h}$, 0 for decreasing momentum transfer. The cause of the separation between the centred reflections h, 0, 0 and 0, $\overline{h}$, 0 remains unknown for the moment.

We now concentrate on the overall diffraction properties of the twinned approximant. Based on the refined lattice parameters, we found extinction rules similar to those of the decagonal phase: the characteristic extinction rule for the decagonal phase is [6]

$$h_1h_2\overline{h_2h_1}h_5 : h_5 = 2n + 1 \tag{1}$$

while we find for the twinned crystal (monoclinic notation)

$$h\overline{h}l : l = 2n + 1. \tag{2}$$

Not only exactly the same lattice constant c, but also the same diffuse interlayers for a doubled lattice constant c as for the decagonal phase were found, the latter using an imaging plate at HASYLAB. Taking the equivalent notation into account ($21, 21, 0 \longleftrightarrow 10\overline{1}\overline{1}0$; $13, 13, 0 \longleftrightarrow 00\overline{1}\overline{1}0$; $8, 8, 0 \longleftrightarrow 10000$; $5, 5, 0 \longleftrightarrow \overline{1}0\overline{1}\overline{1}0$; $3, 3, 0 \longleftrightarrow 20110$), the similarities are remarkable.

Additionally, a hint at some c-axis distortion in our sample was found: the 0, 0, 2 ω-scan shows some structure, which is unexpected in the twinning model. The most probable explanation would be a mismatch for the c-axes between the five (or ten) twinned domains due to zoning.

Finally, first measurements were done on the annealed and quenched sample: figure 6 shows the 10000 quasicrystal reflection of both samples in comparison. The striking difference from the sample discussed previously is the diffuse peak at $Q_{\parallel} \simeq 1.655$ Å^{-1} for sample 2, while sample 1 revealed four separate peaks in the same range of momentum transfers. Sample 2 has overall tenfold symmetry for the 10000 reflection and its symmetry

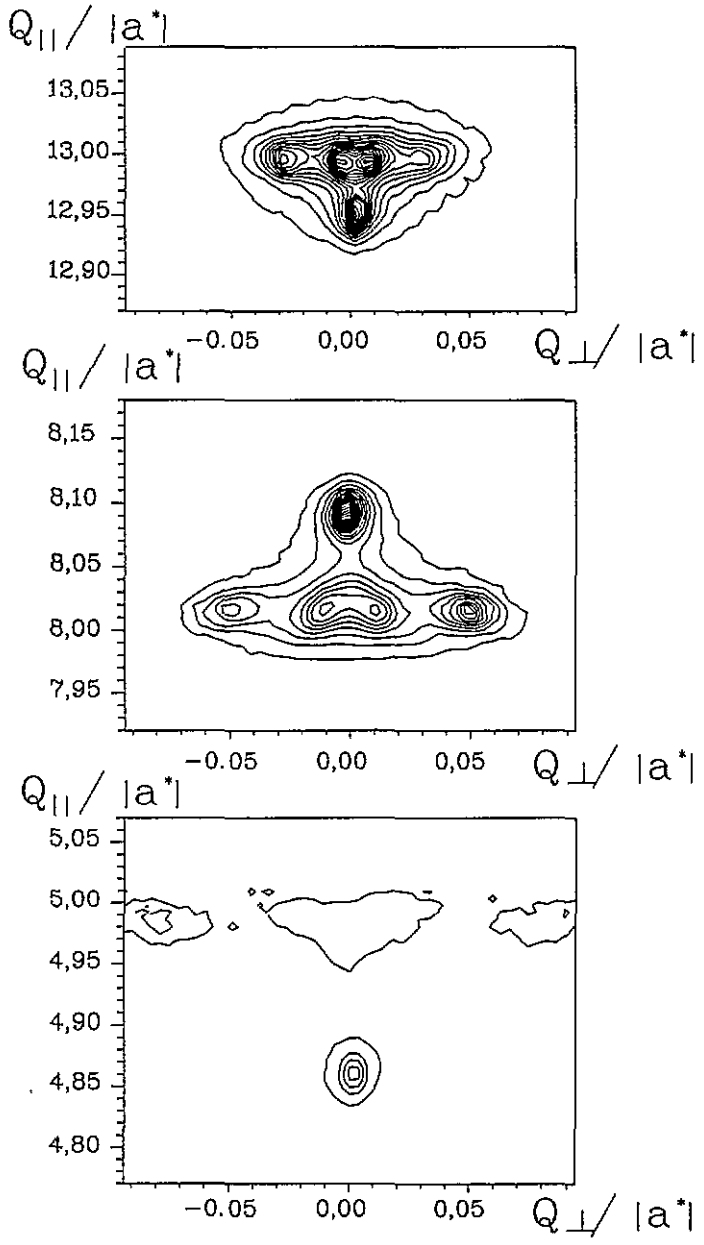

Figure 5. *Q*-space contour plots (D3) in the tenfold-symmetry plane: the reflections *5, 0, 0, 8, 0, 0* and *13, 0, 0 recorded at D3. They all reveal a characteristic splitting. Note the* increasing distances with decreasing momentum transfer.

relatives, too. We conclude that sample 2 is in a quasicrystalline state; at least, the conclusion appears to be more justified than for sample 1.

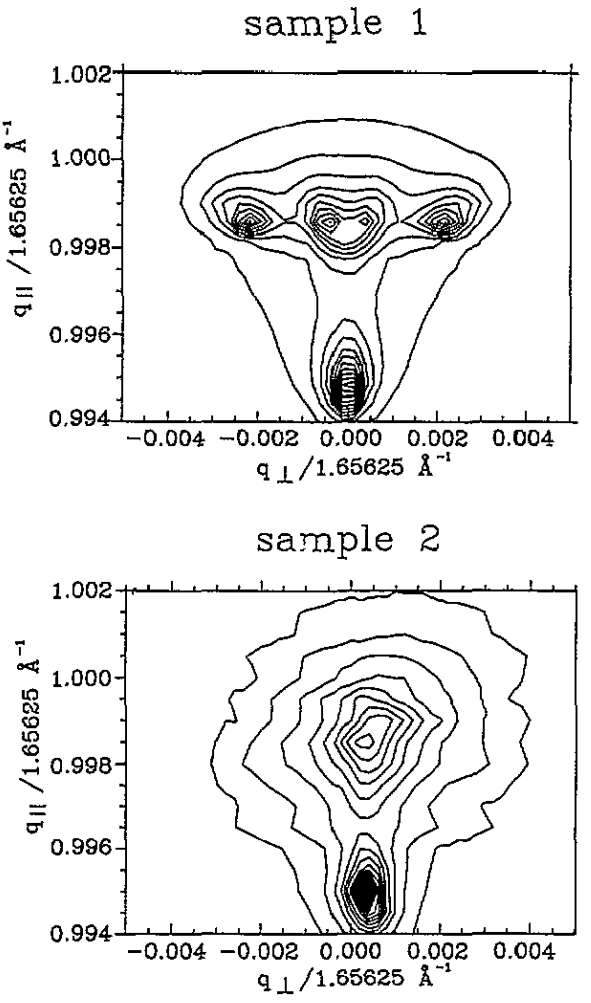

Figure 6. Comparison: the 10000 reflection of sample 1 (slow solidification) and sample 2 (rapid solidification). Sample 2 exhibits diffuse diffraction phenomena. Measured at the rotating anode (Kiel).

5. Conclusions

The characteristic properties of a twinned high-order (5, 7) approximant to the decagonal phase visible in an x-ray scattering experiment are reported. For identification of the twinned state very good Q resolution is indispensible. The conventionally used crystallographic data-collecting mode employs an open detector slit for collecting integrated intensities and does not resolve the characteristic splitting in the twinned state in detail. Compared to the decagonal phase almost identical peak positions result for the twinned system. We found a c-axis lattice constant identical with that of the decagonal phase. In addition, the diffuse scattering and extinction rules are very similar to those of the decagonal phase. As a consequence, great care has to be taken when interpreting diffuse scattering of decagonal'single' crystals without sufficient consideration of resolution effects [11]. The investigated crystal probably has the space group *Ccmm*, which is a subgroup of

the space group $P10_5/mmc$ and the transition twinned approximant $\longleftrightarrow$ decagonal phase is crystallographically allowed. Our results reveal similar lattice constants for the approximant phase as reported elsewhere, but also a slight deviation from an ideal incoherently twinned system is reported. c-axis distortion, which was also found, cannot overcome the discrepancy.

We conclude that the understanding of discrepancies in the twinning model can give a hint at the crystal structure of the periodic approximant. A description of the approximant in terms of a distorted ideal decagonal quasicrystal may be the key to understanding the structural properties of the stable decagonal phase.

Acknowledgments

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