

Solving Approximant Structures Using a “Strong Reflections” Approach

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A new general approach for solving τ -related approximants in an inflation series is derived. The strongest reflections from an approximant with known structure are used to deduce the structure of other approximants in the series. The structure model deduced in such a way is close enough to the true structure and a more accurate structure can be obtained from the refinement of such a model. The method is applied to $m\text{-Al}_{13}\text{Co}_4$, ($C2/m$, $a = 15.173 \text{ \AA}$, $b = 8.109 \text{ \AA}$, $c = 12.349 \text{ \AA}$ and $\beta = 107.84^\circ$) [1] and the inflation related $\tau^2\text{-Al}_{13}\text{Co}_4$ [2].

Keywords Quasicrystals; approximants; structure prediction; τ -inflation; crystallography

Introduction

Unlike most crystals, quasicrystals and their approximants come in series of related structures. Many authors have compared the approximants in a series and even solved one approximant from model-building its atomic structure based on another approximant in its series [3].

Both quasicrystals and approximants have distinct patterns of very strong reflections at about 2 \AA resolution, related to the typical inter-atomic distance in alloys of around 2.4 \AA . This raises several interesting questions:

How much structural information do these strong reflections carry? Is this information sufficient for solving (not refining) a crystal structure?

As the strongest reflections are always distributed in the same way and at the same related positions in reciprocal space for all structures in an inflation series, is it possible to get the next structure in such a series by just re-indexing reflections according to the rescaling, thus solving the structure without actually doing the diffraction experiment? Here we introduce a new approach to solve the atomic structures of series of approximants based on the similarities of the distribution of strong reflections in reciprocal space.

Deducing a Structure Model of $m\text{-Al}_{13}\text{Co}_4$

To investigate the first two questions it is necessary first to look at a structure that has already been solved. In this case we chose $m\text{-Al}_{13}\text{Co}_4$ with $a = 15.173(1) \text{ \AA}$, $b = 8.1090(3) \text{ \AA}$,

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TABLE 1 The 11 Strongest Unique Reflections Used in Calculating the Density Maps

m-Al ₁₃ Co ₄			τ^2 -Al ₁₃ Co ₄			Amp.	Phase	d-spacing /Å	Multiplicity
h	k	l	h	k	l				
2	0	-6	6	0	-16	596	0	2.06	2
6	0	2	16	0	5	501	180	2.03	2
2	0	5	6	0	13	569	0	2.06	2
6	0	-5	16	0	-13	623	180	2.02	2
8	0	-2	20	0	-5	535	0	1.90	2
Average int.						565			
6	2	-3	16	2	-8	644	180	2.07	4
4	2	3	10	2	8	659	180	2.02	4
6	2	0	16	2	0	688	180	2.07	4
0	2	5	0	2	13	607	0	2.04	4
4	2	-5	10	2	-13	595	180	2.01	4
Average int.						639			
0	4	0	0	4	0	963	0	2.03	2

$c = 12.349(1)$ Å and $\beta = 107.84(1)^\circ$, space group $C2/m$ [1]. This structure is chosen because it is a member of an inflation series where the τ^2 , τ^3 and τ^4 structures are known to exist [2]. None of the inflated structures have been solved yet, but structure models have been suggested for τ^2 -Al₁₃Co₄ [3–5]. The Al-Co system is especially interesting because it has many related quasicrystals.

From the atomic positions published [1] we calculated the structure factor amplitudes and phases using the program LAZY [6]. The strongest reflections are located at 2 Å resolution and they are regularly distributed over a sphere in reciprocal space. The strongest reflections with their amplitudes, phases and d-spacings are shown in Table 1. The program 3D-Map [6] was used to generate a density map from only these strongest reflections and to extract atomic coordinates. Atomic layers are located on sections perpendicular to the b -axis.

Results

The electron density map of m-Al₁₃Co₄ calculated from only the 11 strongest unique reflections listed in Table 1 is shown in Fig. 1, top row. All peaks are well resolved and the positions of the peaks are remarkably close to those in the correct structure (bottom row in Fig. 1), as derived from X-ray crystallography [1]. The five highest peaks in the density map correspond to the five cobalt atoms. 19 out of the 20 Al atoms were found, most of them within 0.3 Å from their correct positions. Two atoms were off by 0.5–0.6 Å and one atom was split into two in the density map (Fig. 1, top row).

The main deviations of our model deduced from the 11 strongest reflections from the X-ray model [1] are found at $y = 0$ and $y = 0.5$. Since all the 11 reflections used have even h indices, so the density map has only a periodicity of $a/2$ along the a -axis while in the true structure the periodicity is a (Fig. 1). The correct structure can be obtained by refining the model against a complete set of structure factor amplitudes obtained either by electron diffraction or X-ray diffraction.

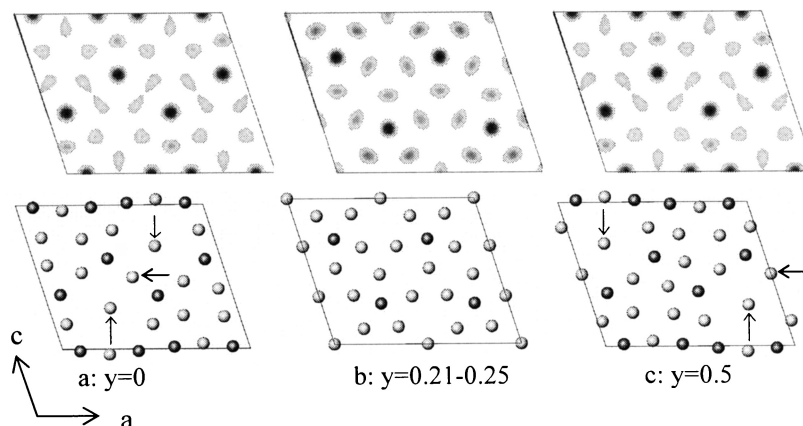


FIGURE 1 Comparison of our calculated (top) and true (i.e., from X-ray) atomic layers (bottom) of $m\text{-Al}_{13}\text{Co}_4$. In the top figures red represents the highest density. In the bottom figures blue is cobalt and yellow is aluminium. The arrows indicate the atoms not found or split in the calculated density map. The stacking sequence is a-b-c-b-a.

Deriving a Structure Model for $\tau^2\text{-Al}_{13}\text{Co}_4$

To see if it is possible to get the next structure in a series by just re-indexing reflections according to the rescaling, we have studied the τ^2 related structure $\tau^2\text{-Al}_{13}\text{Co}_4$ (also known as Al_3Co , space group $P2/m$ $a = 39.863(5)$ Å, $b = 8.139(1)$ Å, $c = 32.208(6)$ Å, $\beta = 107.96(2)^\circ$ [4]) which has a unit cell that is τ^2 times larger than $m\text{-Al}_{13}\text{Co}_4$ along the a and c axis, while the b axis and the β angle are similar. By re-indexing the reflections used in $m\text{-Al}_{13}\text{Co}_4$ according to this unit cell change while keeping the phases, as suggested by Zou et al. [8], the Fourier transform should give a good structure prediction. For $\tau^2\text{-Al}_{13}\text{Co}_4$ the strong reflections in $h0l$, $hk0$ were taken from [3]. The indices in $m\text{-Al}_{13}\text{Co}_4$ and $\tau^2\text{-Al}_{13}\text{Co}_4$ are related as numbers in Fibonacci's series; $6 \approx 2 \cdot \tau^2$, $8 \approx 3 \cdot \tau^2$, $13 \approx 5 \cdot \tau^2$, $16 \approx 6 \cdot \tau^2$ and so on. The k indices are left unchanged because the b axis is always 8.1 Å. The $h2l$ indices for $\tau^2\text{-Al}_{13}\text{Co}_4$ were derived by us, using the rule found for $h0l$. In a study on $\kappa\text{-Al}_{76}\text{Cr}_{18}\text{Ni}_6$ and $\lambda\text{-Al}_4\text{Mn}$ [8] it was found that the structure factor phases of τ -inflated strong reflections were identical. We assumed that the phases of the strong reflections at 2 Å in $m\text{-Al}_{13}\text{Co}_4$ are the same as those of the τ^2 -related strong reflections in $\tau^2\text{-Al}_{13}\text{Co}_4$. Table 1 shows the re-indexed reflections with the amplitudes and phases the same as those for $m\text{-Al}_{13}\text{Co}_4$.

Results

By looking at the list of re-indexed reflections it is observed that the C-centering is maintained when only using the strong reflections, even though the space group is determined as $P2/m$ [4]. Although $m\text{-Al}_{13}\text{Co}_4$ crystallizes in $C2/m$ and $t2\text{-Al}_{13}\text{Co}_4$ in $P2/m$, their diffraction patterns are very similar. The reflections with $h+k = 2n+1$ that are forbidden by the C-centering are all very weak in $\tau^2\text{-Al}_{13}\text{Co}_4$. The $\tau^2\text{-Al}_{13}\text{Co}_4$ structure has not been solved yet, but in Fig. 2 our structure prediction is compared with the model of Li and Hiraga [4]. There is an almost perfect one to one relation between the atom positions in our density map and the model, although the assignment of cobalt atoms could differ at some

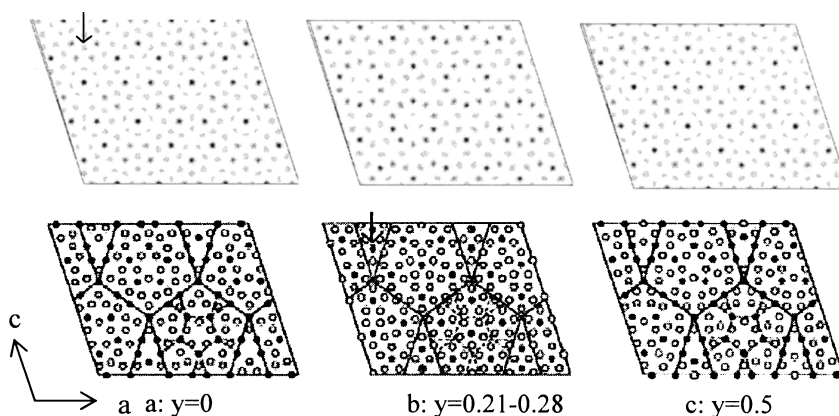


FIGURE 2 Top row: Density maps of τ^2 - $\text{Al}_{13}\text{Co}_4$ calculated from the reflections in Table 1. Bottom row: structure model of τ^2 - $\text{Al}_{13}\text{Co}_4$ proposed by Li and Hiraga [4]. The main discrepancy is marked with an arrow; an atom is placed in different layers in the two models.

places. The left and right halves of the unit cell are nearly identical in the model by Li and Hiraga (i.e. if there is an atom at xyz there is a similar atom at $x + 1/2, y, z$). In our density map these two halves are identical, because we have not used any of the weak reflections with $h = 2n + 1$.

Discussion and Conclusion

We have shown that the strong reflections from quasicrystal approximants carry enough information for solving the structure. It may be surprising already that 11 unique reflections can generate 19 out of the 20 unique atoms in $\text{mAl}_{13}\text{Co}_4$, but it is truly remarkable that over 50 unique atoms in τ^2 - $\text{Al}_{13}\text{Co}_4$ can be located from a density map calculated from only 11 unique reflections. The apparent break of the rule of thumb that one needs at least one reflection for each parameter is due to the many pseudo symmetries in this kind of structures. We have also shown that due to the similarities between structures in an inflation series it is possible to get the next structure in a series simply by rescaling a known structure in reciprocal space.

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Appendix

TABLE A1 Comparing Coordinates for Al₁₃Co₄. To the Left the Coordinates as Found from the Density Map Generated from the 11 Strongest Reflections, and to the Right as Published in an X-ray Structure Solution [1]

Atom	Deduced in this paper			Relative peak height	Atom	X-ray structure			Deviation Calculated distance/Å
	x	y	z			x	y	z	
Co	0.318	1/4	0.278	24.6	Co5	0.3204	0.2821	0.2787	0.2256
Co	0.904	0	0.616	24.6	Co4	0.9150	0	0.6201	0.1593
Co	0.404	0	0.616	24.6	Co1	0.3984	0	0.6292	0.2016
Co	0.904	0	0	21.8	Co3	0.9095	0	0.0138	0.1653
Co	0.596	0	0	21.8	Co2	0.5986	0	0.0144	0.1700
Al	0.377	1/4	0.110	17.4	Al 13	0.3728	0.2211	0.1194	0.3113
Al	0.175	1/4	0.110	17.4	Al 14	0.1837	0.2117	0.1059	0.3112
Al	0.175	1/4	0.331	15.5	Al 10	0.1869	0.2248	0.3350	0.2928
Al	0.490	1/4	0.331	15.5	Al 12	0.4986	0.2233	0.3279	0.2292
Al	0.371	1/4	0.486	15.5	Al 11	0.3626	0.2183	0.4786	0.2546
Al	0.457	0	0.829	15.0	Al 2	0.4744	0	0.8263	0.2746
Al	0.957	0	0.829	15.0	Al 4	0.9340	0	0.8241	0.3355
Al	0	1/4	0	14.8	Al 15	0	1/4	0	0
Al	0.921	0	0.233	13.2	Al 7	0.9162	0	0.2236	0.1110
Al	0.695	0	0.229	13.2	Al 8	0.7027	0	0.2339	0.1106
Al	0.772	0	0.086	11.9	Al 3	0.7580	0	0.0363	0.5812
Al	0.772	0	0.429	11.8	Al 5	0.7634	0	0.4688	0.5470
Al	0.440	0	0.424	11.8	Al 1	1/2	0	1/2	1.0820
Al	0.940	0	0.424	11.8	Al 6	0.9344	0	0.4163	0.1134
		Al 9 not seen			Al 9	0.3276	0	0.2862	