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Corresponding author: H. Zhang

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Structure relations in real and reciprocal space of hexagonal phases related to i-ZnMgRE quasicrystals

H. ZHANG*, X. D. ZOU, P. OLEYNIKOV and S. HOVMÖLLER

Structural Chemistry, Stockholm University, SE-10691, Stockholm, Sweden

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The μ_3, μ_5 and μ_7 approximants in Mg-Zn-RE were related in real and reciprocal space. The structure factors of μ_3, μ_5 and μ_7 have quite similar intensity distributions and identical phases for the strongest corresponding reflections. Structure models of any of μ_3, μ_5 and μ_7 can be obtained from any of the others using the strong reflections approach.

1. Introduction

Quasicrystals in Mg-Zn-RE (rare earth) alloys have attracted great interest because this system requires no Al, which otherwise is the main element in the classical icosahedral phases. Several crystalline approximant phases are found in the Mg-Zn-RE systems. Among these approximants, the μ_3, μ_5 and μ_7-MgZnRE all have the same hexagonal space group $P6_3/mmc$, almost the same c parameter ($\sim$8.6 Å), while the a parameters are 14.6, 23.5 and 33.6 Å respectively, i.e. with ratios 3 : 5 : 7. The crystal structures of μ_3 and μ_7 have been solved by X-ray diffraction [1–3], while a structure model for μ_5 was proposed on the basis of the structures of the μ_3 and μ_7 phases [4]. These three hexagonal phases have very similar columnar clusters in the projected atomic arrangements along the [001] direction [4].

The above is from a real space point of view. In reciprocal space, quite reasonable structure models can be obtained using the strong reflections approach [5–7]. In this paper, we compare the reciprocal lattices of μ_3, μ_5 and μ_7 and find out the common features in reciprocal space, and show how these can be used to reconstruct structure models of an approximant from a related one.

2. Relating the reciprocal lattices of μ_3, μ_5 and μ_7

The μ_3, μ_5 and μ_7 in the Mg-Zn-RE alloy systems all have the $P6_3/mmc$ space group (μ_3: $a = 14.6$ Å, $c = 8.6$ Å; μ_5: $a = 23.5$ Å, $c = 8.6$ Å; μ_7: $a = 33.6$ Å, $c = 8.9$ Å). In spite of these different unit cell sizes, their diffraction patterns are strikingly similar (see figure 1 in [4]). Thus, for example reflection (3 3 0) in μ_3 corresponds to

*Corresponding author. Email: hzhang@struc.su.se

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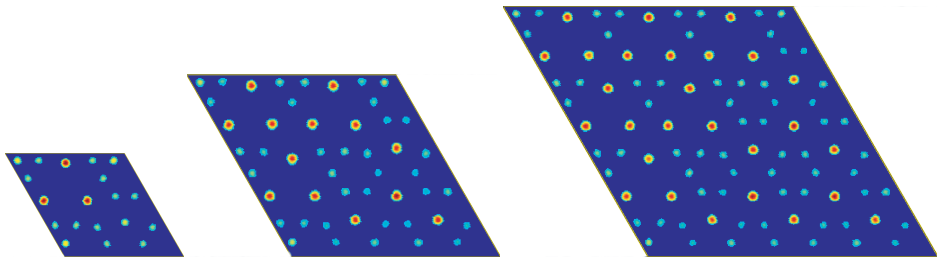


Figure 1. Density maps at $z = 1/4$ layer (a) for μ_3 calculated with 108 unique reflections, (b) for μ_5 calculated with 224 unique reflections and (c) for μ_7 calculated with 279 unique reflections.

(5 5 0) in μ_5 and (7 7 0) in μ_7; (6 0 0) in μ_3 corresponds to (10 0 0) in μ_5 and (14 0 0) in μ_7.

The orientation relationships among μ_3, μ_5 and μ_7 are

$$(3\ 3\ 0)_{\mu3}//(5\ 5\ 0)_{\mu5}//(7\ 7\ 0)_{\mu7}$$
$$(6\ 0\ 0)_{\mu3}//(10\ 0\ 0)_{\mu5}//(14\ 0\ 0)_{\mu7}$$
$$(0\ 0\ 1)_{\mu3}//(0\ 0\ 1)_{\mu5}//(0\ 0\ 1)_{\mu7}$$

The reciprocal lattices of μ_3 and μ_7 are related by a matrix A through

$$(h\ k\ l)_{\mu3} = (h\ k\ l)_{\mu7} \cdot \mathrm{A} \tag{1}$$

The pairs of strong reflections between μ_3 and μ_7 are selected and their indices are used to determine the matrix A, using the curve fitting program LAB Fit [8]. The matrix A is

$$\mathrm{A} = \begin{pmatrix} 0.437 & 0 & 0 \\ 0 & 0.437 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{2}$$

In a similar way, the reciprocal lattices of μ_5 and μ_7 are related by a matrix B through

$$(h\ k\ l)_{\mu5} = (h\ k\ l)_{\mu7} \cdot \mathrm{B} \tag{3}$$

with

$$\mathrm{B} = \begin{pmatrix} 0.718 & 0 & 0 \\ 0 & 0.718 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{4}$$

3. Structure factors of μ_3, μ_5 and μ_7

The structure factors of μ_3, μ_5 and μ_7 were calculated to 1.2 Å resolution with the program LAZY [9] from the atomic coordinates in the literature [1, 2, 4]. In total there are 215, 515 and 1049 unique reflections within 1.2 Å resolution for μ_3, μ_5 and μ_7, respectively. In order to compare the structure factors, the indices of the corresponding reflections in μ_3 and μ_5 were calculated from reflections in μ_7 using equations (1–4). The calculated (h k l) indices for μ_3 and μ_5 were rounded to nearest integer numbers. The deviations between unrounded and rounded indices are one of the differences of μ_7 to μ_3 and μ_7 to μ_5 in reciprocal space. The 30 strongest reflections among the 1049 unique reflections in μ_7 are listed in table 1, together with the corresponding reflections in μ_3 and μ_5. Also the deviations from the exact reciprocal lattice points of μ_3 and μ_5 are listed. The structure factor amplitudes are scaled to a maximum of 1000 for each compound. All those strong reflections in table 1 are at almost the predicted positions in reciprocal space. The related reflections are quite strong in all these three phases. However, the most interesting thing is that these reflections from three different structures have exactly the same crystallographic structure factor phases!

4. Reconstructing structures of μ_3, μ_5 and μ_7 with limited reflections

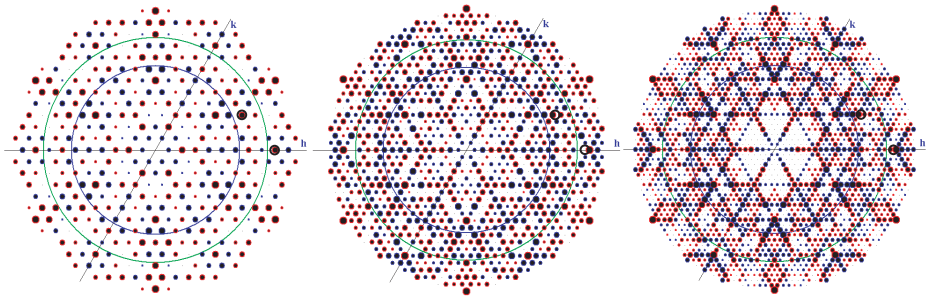
Having noted that it is possible to deduce the amplitudes and phases of the strongest reflections of any of the μ-phases from another, we now proceed to see if it is also possible to obtain a good structure model with these data. In μ_7, 279 strongest unique reflections sum up to 75% of the total amplitudes of all 1049 unique reflections. From 75% of the total amplitudes, we expect it should be possible to obtain an accurate structure model. Using only these 279 reflections, a density map was calculated by 3D inverse Fourier transformation using eMap [10]. The 3D map was sampled with 0.1 Å per pixel along the three main axes. The $z = 1/4$ layer of the calculated map is shown in figure 1c. The density map is clear and has well resolved peaks. It is quite similar with the X-ray model. The atomic positions determined from this density map and those from X-ray diffraction are virtually identical. We found all the atom positions in the density map. The atom positions deviated 0.11 Å on average from the atomic positions in [1]; the maximum deviation was 0.26 Å.

From the 279 strongest reflections of μ_7, we calculated the corresponding reflections in μ_5 and μ_3 as shown for the 30 strongest reflections in table 1. μ_7 has the smallest reciprocal lattice spacing. It is possible that more than one reflection in μ_5 and μ_7 correspond to one reflection in μ_3. This is evident from the *hk*0 reciprocal layers of calculated structure factors of μ_3, μ_5 and μ_7 seen in figure 2. The two unique reflections (20 0 0) and (21 0 0) in μ_7 correspond to (14 0 0) and (15 0 0) in μ_5 but to a single reflection (9 0 0) in μ_3 (indicated by small circles in figure 2); (11 7 0) and (12 7 0) in μ_7 correspond to (8 5 0) and (9 5 0) in μ_5 and only (5 3 0) in μ_3.

From the 279 strongest reflections in μ_7, we derived 279 corresponding reflections in μ_3. These all had non-integer indices, and were rounded to the nearest integer

Table 1. Amplitudes and phases of the 30 strongest unique reflections in μ_7, and the corresponding reflections in μ_3 and μ_5. Dev is the geometric deviations between related reflections in μ_3 to μ_7 and μ_5 to μ_7.

	Structure factors of μ_7					Structure factors of μ_5					Dev	Structure factors of μ_3					Dev
No.	h	k	l	|Fhkl|	Phase	h	k	l	|Fhkl|	Phase	($\times 10^2$ Å^{-1})	h	k	l	|Fhkl|	Phase	($\times 10^2$ Å^{-1})
1	7	7	0	1000	0	5	5	0	1000	0	0.26	3	3	0	762	0	0.93
2	0	0	4	936	0	0	0	4	904	0	0.00	0	0	4	1000	0	0.00
3	0	0	6	830	180	0	0	6	889	180	0.00	0	0	6	832	180	0.00
4	14	14	0	801	0	10	10	0	795	0	0.53	6	6	0	639	0	1.87
5	7	0	3	761	0	5	0	3	791	0	0.15	3	0	3	741	0	0.54
6	21	0	0	697	0	15	0	0	666	0	0.46	9	0	0	445	0	1.62
7	11	0	3	582	0	8	0	3	560	0	0.57	5	0	3	571	0	1.76
8	14	7	3	521	0	10	5	3	494	0	0.40	6	3	3	417	0	1.43
9	11	0	1	433	180	8	0	1	490	180	0.57	5	0	1	509	180	1.76
10	11	0	5	409	180	8	0	5	464	180	0.57	5	0	5	464	180	1.76
11	14	0	6	391	0	10	0	6	404	0	0.31	6	0	6	446	0	1.08
12	0	0	2	389	180	0	0	2	551	180	0.00	0	0	2	395	180	0.00
13	11	0	2	386	0	8	0	2	402	0	0.57	5	0	2	536	0	1.76
14	11	7	0	350	0	8	5	0	324	0	0.51	5	3	0	380	0	1.56
15	18	0	2	347	0	13	0	2	376	0	0.42	8	0	2	395	0	1.22
16	14	0	2	334	0	10	0	2	426	0	0.31	6	0	2	445	0	1.08
17	7	4	2	325	0	5	3	2	390	0	0.66	3	2	2	365	0	2.08
18	10	0	3	322	180	7	0	3	428	180	1.03	4	0	3	401	180	3.38
19	7	4	6	318	0	5	3	6	315	0	0.66	3	2	6	315	0	2.08
20	11	0	6	317	0	8	0	6	331	0	0.57	5	0	6	373	0	1.76
21	7	7	6	302	180	5	5	6	256	180	0.26	3	3	6	127	180	0.93
22	14	4	3	281	180	10	3	3	279	180	0.63	6	2	3	170	180	1.99
23	11	7	4	277	0	8	5	4	275	0	0.51	5	3	4	438	0	1.56
24	10	7	0	266	180	7	5	0	330	180	1.11	4	3	0	333	180	3.68
25	7	4	0	264	180	5	3	0	254	180	0.66	3	2	0	195	180	2.08
26	7	0	6	261	0	5	0	6	258	0	0.15	3	0	6	290	0	0.54
27	15	7	3	258	180	11	5	3	237	180	1.22	7	3	3	246	180	3.82
28	7	0	4	254	0	5	0	4	361	0	0.15	3	0	4	250	0	0.54
29	7	7	2	250	0	5	5	2	211	0	0.26	3	3	2	454	0	0.93
30	14	0	1	244	180	10	0	1	301	180	0.31	6	0	1	407	180	1.08



(a) (b) (c)

Figure 2. The *hk*0 reciprocal layers of calculated structure factors of (a) μ_3, (b) μ_5 and (c) μ_7. Small circles indicate corresponding reflections in the three structures. Red reflections have phase 0°, while blue ones have phase 180°. The large blue and green circles indicate 2.0 and 1.5 Å resolution.

indices. 140 reflections deviate less than 2.78×10^{-2} Å^{-1} (around 35% of the $a_{\mu 3}$* reciprocal axis) from their integer indices in reciprocal space. 108 out of those 140 reflections are unique since often two or more reflections in μ_7 correspond to one in μ_3, as mentioned above. They all had exactly the same phases as in μ_7. The 108 unique reflections are the common reflections between μ_3 and μ_7 with the same distributions of amplitudes and phases. We calculated a density map as described above with the 108 unique reflections. The $z = 1/4$ layer of the map is shown in figure 1a. All the atomic positions were found in the density map. The positions deviated 0.07 Å on average from atomic positions in the X-ray structure [4]; the maximum deviation was 0.20 Å.

The same procedure was performed to reconstruct μ_5 from μ_7. 279 corresponding reflections indices in μ_5 were derived from the 279 strongest reflections in μ_7. 273 reflections deviate less than 2.78×10^{-2} Å^{-1} (57% of the $a_{\mu 5}$* reciprocal axis, approximately 35% of the $a_{\mu 3}$* reciprocal axis) from their integer indices. 268 out of those 273 reflections have the same phases as their corresponding reflections in μ_7. Then these 268 reflections were merged to 224 unique μ_5 reflections. A density map was calculated from these 224 reflections. The layer with $z = 1/4$ of the map is shown in figure 1b. Also here, all the atoms were found in the density map. Their positions deviated 0.12 Å on average from the atomic positions in reference [2]; the two largest deviations were 0.57 and 0.21 Å. From the above reconstructions of μ_3, μ_5 and μ_7 structure models, we see that good structure models of a series of approximants can be constructed, once one member in the series is known.

5. Conclusion

Based on the close similarities in reciprocal space of the approximants μ_3 and μ_5 with μ_7, structure models of μ_3 and μ_5 were obtained. This is a general method for solving approximant structures from closely related known structures.

Acknowledgments

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