Real space structure refinement of the basic Ni-rich decagonal Al-Ni-Co phase.

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Abstract. Structure refinement of the basic Ni-rich Al-Ni-Co decagonal phase was performed in physical space. Statistical approach was used to derive the structure factor. Rhombic Penrose tiling with an edge length of 10.28 Å was chosen as a reference lattice. The best-fit structure model with 106 parameters and 2767 reflections gives R = 12.3% and wR = 6.2%. The observations-to-parameters ratio is high - 26.1 Density and chemical composition of the resulting structure are very close to experimental values.

1. Introduction
There are 8 different decagonal phases reported in the Al-Ni-Co system [1 and references therein]. The only phase, for which a qualitative structure refinement was performed, is the so called basic Ni-rich phase. In the majority of published papers a higher-dimensional approach i.e. the atomic surface modelling method is used for the optimization [2,3]. We present the results of a real space structure refinement of the basic Ni-rich decagonal phase based on a diffraction data set without referring to the higher-dimensional properties of decagonal quasicrystals.

Structure factor which was used for the modelling process was calculated on the basis of a statistical method described in [4,5]. We used rhombic Penrose tiling as a reference lattice. Initial atomic positions were set in the vertices of rhombuses divided four times with obedience to the inflation rules. Additionally atoms were divided into 24 groups. For each group we optimized probabilities of vertices occupation, TM concentration, a shift from initial position and two components of Debye-Waller coefficient. Two components are necessary because of the anisotropy of the structure. One component is associated with xy plane, i.e. quasiperiodic plane, the other component is associated with z direction, i.e. periodic direction. All together 106 parameters were refined. The optimization was performed on a set of 2767 symmetrically independent reflections (merged in 10/m Laue group) taken by a 4 four-circle diffractometer Huber at beamline D3, HASYLAB. The chemical composition of the sample was checked to be Al₇₀.₆Ni₂₂.₅Co₆.₇ [2].

The diffraction data set is larger in comparison to our previous paper [6] (only 451 symmetrically independent reflections), which makes the refinement much more reliable.
2. Initial structure model

Structure of the basic Ni-rich decagonal Al-Ni-Co phase is known to consist of a periodic set of quasiperiodic planes stacked along the z direction. There are two planes within one period of the z axis. These planes are related by a screw axis 10\_5. The shortest interatomic distances in the structure of the basic Ni-rich decagonal Al-Ni-Co can be determined using a Patterson map [2]. These distances scale in exactly the same way as distances between vertices of Penrose tiling, providing that proper z coordinate is chosen for these vertices. Thus we assumed that the projection of the structure along z axis results in Penrose tiling.

Our structure units are thick and thin rhombuses of Penrose tiling divided three times with obedience to the inflation rules. All positions from the 0-th, 1-th, 2-nd, and 3-rd division are occupied in the initial model. We, however, also put atoms in several positions of the fourth division to fulfil the density restriction. 70 atoms decorating our structure units were divided into 24 groups. This division was made according to adherence rules for rhombuses [4,5], overlapping rules for kite-clusters [7], and an assumption that the decoration is symmetric with respect to the longer diagonal of thick rhombus and shorter of the thin one. The adherence rules were used for all decorating atoms since they are essential for the correctness of the structure factor calculation. Also the assumption of a symmetric decoration was strictly obeyed. The overlapping rules for clusters were used solely for atoms from the 0-th, 1-th, 2-nd, and 3-rd division, which form a skeleton of the structure. The division of atoms into groups is illustrated in the figure 1.

![Figure 1. The division of atoms into 24 groups](image)

The edge length of our structure units (a) is 10.29 Å and the period along the z axis (c) 4.09 Å. Circles and squares distinguish the layers at z = 0.25c and z = −0.25c respectively. Dark grey symbol colour denotes TM atoms light grey Al/TM atoms and white Al atoms. Some positions are marked by additional circle. The results of structure refinement are given for these positions. In the initial model all occupation probabilities are equal to 1. Atoms from 0-th, 1-th, 2-nd, and 3-rd division are either Al or TM (white or dark grey symbols, groups 1-13). The initial concentration of TM atom at the positions of 4-th division is 0.25 (light grey symbols, groups 14-24). Atoms in the group 22 are slightly moved out of the edge, inside the thick rhombus. This is why there is no atom from the group 22 in the thin rhombus. A detailed explanation of this assumption is given in the paragraph 5.

3. Structure factor

The structure factor was calculated in the real space on the basis of statistical approach. The concept of average unit cell for Penrose tiling and a detailed derivation of the structure factor for any decoration is extensively studied in [5]. Here we shall only show the resulting formula:
\[ F(\mathbf{k}) = D_D \sum_{\alpha} \left[ F_1^\alpha \sum_{i=1}^n f_i D_i p_i \exp(\mathbf{i k} \cdot \mathbf{r}^i) + F_2^\alpha \sum_{i=1}^n f_i D_i p_i \exp(\mathbf{i k} \cdot \mathbf{r}^i) \right] \]

\( F_{\text{TLS}} \) is the Fourier transform of a triangular probability distribution associated with thin (S) or thick (L) rhombus at orientation \( \alpha \) (there are 10 different possible orientations of each rhombus[7]), \( \mathbf{r}^{\alpha}_{(s)} \) is the position of an atom in a given structure unit at orientation \( \alpha \), \( n_{\text{TLS}} \) is the number of atoms decorating thick or thin rhombus, \( \mathbf{k} \) is a scattering vector, \( f_{(s)} \) is the average atomic form factor. A formula for \( f_{(s)} \) reads:

\[ f_{(s)} = p_{\text{calc}}(p_{\text{TM}} f_{\text{TM}} + (1 - p_{\text{TM}}) f_{\text{Al}}) \]

\( p_{\text{calc}} \) is the occupation probability of a given vertex by an atom, \( p_{\text{TM}} \) is concentration of TM atoms at a given position, \( f_{\text{TM}} \) is the atomic form factor for TM atoms (weighted Co and Ni), \( f_{\text{Al}} \) atomic form factor for Al atoms. \( D_{(s)} \) is the Debye-Waller factor:

\[ D_{(s)} = \exp\left(-\frac{1}{16\pi^2}(k_x^2 + k_y^2)b^{\alpha}_{(s)} - \frac{1}{16\pi^2}k_z^2b_{(s)}\right) \]

\( b_{(s)} \) is the average displacement parameter in the quasiperiodic plane, \( b_z \) is the displacement parameter in the \( z \)-direction. A relation between these parameters and and the square mean shift of the atom from the equilibrium position \( \langle u_{(s)} \rangle \) reads:

\[ b_{(s)} = 8\pi^2 \langle u_{(s)} \rangle \]

\( D_D \) is a phason Debye-Waller factor. Details on calculating perpendicular components of the scattering vector can be found in [5]:

\[ D_D = \exp\left(-\frac{1}{16\pi^2}(k_x^2 + k_y^2)b_{p_{\text{ph}}}\right) \]

where \( b_{p_{\text{ph}}} \) is the phason displacement parameter.

4. Optimized function

We used a conjugated gradient minimization algorithm. The optimized function reads:

\[ \Delta = wR^2 + PF_1 + PF_2 + PF_3 + PF_4 \]

where:

\[ wR^2 = \frac{\sum_{i}^{N_{\text{obs}}} \left( F_{\text{obs}}^i - F_{\text{calc}}^i \right)^2 \sigma^2}{\sum_{i}^{N_{\text{calc}}} \left( F_{\text{calc}}^i \right)^2 \sigma^2} \]

\[ PF_1 = C_i \sum_{j}^{N_{\text{calc}}} (\delta_{\text{TM}}^j + \delta_{\text{obs}}^j) \]

\[ \delta_{\text{TM}}^j = \begin{cases} 0; & p_{\text{TM}}^{j,\text{calc}} \leq 0.1 \\ \left\langle p_j \cdot p_{\text{TM}}^{j,\text{calc}} \right\rangle; & p_{\text{TM}}^{j,\text{calc}} < 0 \\ \left\langle p_j \cdot (1 - p_{\text{TM}}^{j,\text{calc}}) \right\rangle; & p_{\text{TM}}^{j,\text{calc}} > 1 \end{cases} \]

\[ \delta_{\text{obs}}^j = \begin{cases} 0; & \left\langle p_j \cdot \left( 1 - p_{\text{TM}}^{j,\text{calc}} \right) \right\rangle \leq 0.1 \\ \left\langle p_j \cdot \left( 1 - p_{\text{TM}}^{j,\text{calc}} \right) \right\rangle; & \left( 1 - p_{\text{TM}}^{j,\text{calc}} \right) > 0 \end{cases} \]
\[ PF_2 = C_2 \sum \left( \delta_{xy}^i + \delta_z^i \right) \]
\[ PF_3 = C_3 (d_i - d_i^*)^2 \]
\[ PF_4 = C_4 (c_i - c_i^*)^2 \]

where \( F_{\text{obs}} \) and \( F_{\text{calc}} \) are the amplitudes of observed and calculated structure factor respectively, \( \sigma \) is the standard deviation of a given diffraction peak, \( N_{\text{peaks}} \) is the number of diffraction peaks in the data set and \( N_{\text{atoms}} \) is the number of atoms decorating our structure units, \( d_i \) and \( d_i^* \) are the calculated and theoretical concentration of TM atoms respectively, finally \( c_i \) and \( c_i^* \) are the calculated and theoretical point density. \( PF_1, PF_2, PF_3, PF_4 \) keep the concentration of TM atoms, displacement coefficients, chemical composition and point density respectively in the physical boundaries. Numbers \( C_1, C_2, C_3, C_4 \) are the weights of a given component in the optimized function.

5. Refinement results

The results of optimization are given in the table 1.

| Gr. | x[Å] | y[Å] | z[Å] | \( \Delta x \)[Å] | \( \Delta y \)[Å] | \( b_x \)[Å^2] | \( b_y \)[Å^2] | \( p_{\text{calc}} \) | \( p_{\text{PM}} \) |
|-----|------|------|------|-----------------|-----------------|--------------|--------------|--------------|--------------|
| 1   | 0.000| 0.000| 1.023| *0.000          | *0.000          | 2.6(2)       | 3.8(1)       | *1.00        | *0.00        |
| 2   | 3.180| 9.786| -1.023| *0.000         | *0.000          | 0.58         | 0.49         | *1.00        | *1.00        |
| 3   | 5.145| 3.735| -1.023| 0.082          | *-0.253         | 1.2(1)       | 2.8(2)       | 0.79         | *0.00        |
| 4   | 1.965| 6.051| 1.023 | 0.026          | *0.079          | 0.19         | 0.41         | *1.00        | 0.75         |
| 5   | 3.180| 2.315| -1.023| -0.062         | 0.130           | 0.43         | 0.37         | *1.00        | *1.00        |
| 6   | -3.931| 0.000| -1.023| -0.08(4)       | *0.000          | 2.0(1)       | 0.3(1)       | *1.00        | *1.00        |
| 7   | 0.751| 2.315| -1.023| 0.033          | *0.100          | 0.4(1)       | 3.7(2)       | 0.84         | *0.00        |
| 8   | 2.428| 0.000| -1.023| -0.130         | *0.000          | 0.18         | 5.0(2)       | *1.00        | *0.00        |
| 9   | 2.717| 3.735| 1.023 | 0.14(1)        | 0.002           | 0.66         | 4.6(2)       | *1.00        | *0.00        |
| 10  | 2.428| 7.481| -1.023| 0.003          | *0.008          | 0.5(1)       | 5.5(3)       | 0.87         | *0.00        |
| 11  | 4.394| 1.430| 1.023 | -0.144         | -0.16(1)        | 0.8(1)       | 4.4(1)       | 0.85         | *0.00        |
| 12  | 4.394| 6.051| 1.023 | -0.006         | *0.019          | 0.01         | 4.9(3)       | *1.00        | *0.00        |
| 13  | -4.394| 1.430| 1.023| 0.154          | -0.179          | 0.01(1)      | 2.2(1)       | *1.00        | *0.00        |
| 14  | 3.180| 5.166| -1.023| -0.11(1)       | -0.19(1)        | 2.4(2)       | 2.0(3)       | *1.00        | 0.21         |
| 15  | 5.886| 1.430| -1.023| 0.025          | *-0.077         | 2.3(2)       | 0.7(1)       | 0.4(1)       | 0.2(1)       |
| 16  | 1.965| 1.430| 1.023 | -0.191         | -0.00(1)        | 0.2(1)       | 0.2(1)       | *1.00        | 0.23         |
| 17  | -5.608| 2.315| -1.023| 0.58(1)        | 0.08(2)         | 1.4(2)       | 2.4(1)       | 0.50         | 0.26         |
| 18  | -2.428| 0.000| 1.023 | 0.160          | *0.000          | 0.6(1)       | 0.1(1)       | *1.00        | 0.49         |
| 19  | -8.325| 1.554| -1.023| 0.175          | -0.016          | 0.51         | 0.3(1)       | *1.00        | 0.71         |
| 20  | -12.255| 1.430| 1.023| -0.12(1)       | 0.23(2)         | 1.2(1)       | 0.8(2)       | 0.50         | 0.42         |
| 21  | 4.857| 0.000| -1.023| 0.09(3)        | *0.000          | 1.8(3)       | 1.0(2)       | 0.4(1)       | 0.0(1)       |
| 22  | -3.931| 2.861| -1.023| -0.52(3)       | -0.27(2)        | 1.0(2)       | 1.5(2)       | 0.23         | 0.2(1)       |
| 23  | -7.862| 4.620| 1.023 | -0.72(2)       | 0.15(2)         | 0.9(2)       | 1.4(3)       | 0.39         | 0.20         |
| 24  | -11.216| 0.000| 1.023| -0.25(2)       | *0.000          | 2.3(3)       | 1.1(2)       | 0.27         | 0.00         |

In columns x, y, z the positions of ideal Penrose tiling are given. In \( \Delta x \), \( \Delta y \) columns components of the shift vectors from these ideal positions are listed. In the table 1 shift vectors are given for atoms representing a group (marked with additional black circle in the figure 1). Shifts for other atoms in a
given group can be obtained by a proper rotation of the listed shift vectors. Columns $b_{xy}$ and $b_{yz}$ contain the values of Debye-Waller coefficients, whereas in $p_{calc}$ and $p_{TM}$ columns the occupation probability and TM concentration are given respectively.

Values marked with (*) have not been optimized. For shift vectors there are several reasons for which a parameter is not optimized. Atoms in the first two groups decorate the vertices of our structure units, which cannot be shifted. In some other groups the $y$ direction of a shift vector is not optimized. Atoms decorating edges or symmetry axes of the structure units can only move along them. Therefore, if an atom decorates an edge of a structure unit, then the $y$ component of the shift vector is related to the $x$ component (which was optimized) by a tangent function. If, on the other hand, an atom decorates a symmetry axis of a structure unit, then the $y$ component of the shift vector is fixed to zero. Above restrictions for shift vectors are required for correctness of structure factor calculation. Group number 22 is an exception. It showed large Debye-Waller coefficients already in the first steps of the refinement. Therefore these atoms were artificially slightly moved out of the edge, inside the thick rhombus. Then we allowed optimization of the position. This proved to be effective, because the refined values of Debye-Waller coefficients are reasonable, and the refined positions are still inside the thick rhombus, which guarantees the correctness of the structure factor calculation.

For some groups also the TM concentration or occupation probabilities have not been refined. If in the first steps of optimization the occupation probability or the TM concentration for a given group was smaller than 0.05 or greater than 0.95, then in the next steps these parameters were set to 0 and 1 respectively and not optimized.

If for an optimized parameter in table 1 a standard deviation is not given in the bracket, then this means, that it is lower than 0.001 for shift vectors or 0.01 for probabilities and Debye-Waller coefficients.

A part of the refined structure is shown in the figure 2.

**Figure 2.** Refined structure

Dark grey circles denote TM atoms, light grey Al/TM atoms and white Al atoms. Black dots indicate ideal Penrose tiling positions. Figure 2a shows a projection of the structure along the $z$ axis. Figures 2b and 2c show the layers at $z = 0.25c$ and $z = -0.25c$ respectively. The edge length (black lines in the figures 2b and 2c) was refined to be 10.29 Å and the period $c$ along the $z$ axis 4.09 Å.
Shifts from ideal Penrose tiling positions are rather small and not greater than 8% of the edge length of rhombuses (and in most cases not greater than 4%). Generally shifts for atoms from first three inflation divisions (groups 1 – 13), which form a ‘skeleton’ of the structure are much smaller than for atoms from fourth division (groups 14 – 24).

Occupation probabilities for these skeleton atoms are 1 in most cases and always greater than 0.75. For other groups partial occupation is common. Similarly TM concentration is also well defined for skeleton atoms. Only for one group its value is not equal to 0 or 1. For other groups mixed occupation is possible. A sum of occupancy probabilities for pairs of atoms indicated by pairs of light grey circles, which touch each other or overlap in figures 2b and 2c, is lower than one. These are flip positions. In each tile atoms occupy either first or second position. If there are any distances shorter than 2.4 Å, then a sum of occupation probabilities of atom pairs revealing to short interatomic distance is lower than 1.

In the resulting structure there is a certain degree of disorder within the structure units - thin and thick rhombuses. This could be called a local or short-range disorder. On the other hand, these rhombuses form the Penrose tiling, thus, in our approach, the structure is also perfectly long-range ordered.

Debye-Waller coefficients ($b_{xy}$ and $b_z$) for most groups are smaller than 3 Å$^2$, which is an acceptable value for inorganic materials. Greater values may indicate a certain degree of static disorder in the structure. Some $b_z$ i.e. the component associated with $z$ direction exceed the value of 3 Å$^2$. This could mean that the atomic layers of the structure are puckered rather than flat. In [1] even an 8 Å superstructure is assumed. This means that the period along $z$ axis is doubled. However, there are no half-integer reflections in the diffraction pattern, thus in experiment only an average 4 Å structure is observed. In this approach larger $b_z$ values result from overlapping layers of the superstructure having opposite $z$ displacements. In our paper only the average 4 Å structure is investigated.

A phason displacement parameter $b_{Ph}$, extinction parameter $g$ and scale factor between the calculated and measured diffraction pattern were the global parameters optimized. A total number of parameters refined was 106 and the observations-to-parameters ratio is high and equal 26.1. We obtained $R = 12.3\%$ and the $wR = 6.2\%$. Global parameters, $R$ and $wR$ values calculated for different numbers of strongest reflections are listed in the table 2. The stability of our solution was also checked. In the last steps of the refinement $C_3$ and $C_4$ for $PF_3$ and $PF_4$ were set to 0. Despite that, the refined structure has the exact chemical composition Al$_{70.7}$TM$_{29.3}$ (chemical composition of the sample was measured to be Al$_{70.6}$TM$_{29.4}$ [1]). The point density of our structure is 0.0656 Å$^{-3}$ and overall density 3.94 g/cm$^3$. Experimental values are 0.0661 Å$^{-3}$ and 3.94 g/cm$^3$ respectively. The $F_{calc}/F_{obs}$ plot for the final structure in the logarithmic scale is shown in the figure 3.

| $b_{Ph}$ [Å$^2$] | 0.40(4) |
|------------------|----------|
| $g$              | 2.(9)∙10$^{-5}$ |
| $R$ [%] all 2767 reflections | 12.3 |
| $wR$ [%] all 2767 reflections | 6.2 |
| $R$ [%] I$>$3σ, I=1,194 reflections | 4.3 |
| $wR$ [%] I$>$3σ, I=1,194 reflections | 5.7 |
| $R$ [%] I$>$10$^{-4}$ I$<$max 837 reflections | 4.1 |
| $wR$ [%] I$>$10$^{-4}$ I$<$max 837 reflections | 5.4 |

Figure 3. $F_{calc}/F_{obs}$ plot in logarithmic scale
In comparison to our previous paper [6] the diffraction data set is much larger while the number of refined parameters is similar. Therefore the observations-to-parameters ratio is higher, and whole refinement is more reliable. The division of atoms was slightly changed, and the number of groups was increased from 19 to 24. Debye-Waller coefficients are lower, $R$ and $wR$ values are better even for 837 strongest reflections (table 2), than for 451 reflections in the previous paper. This proves a better structure model choice.

6. Conclusions
In this paper we have described the results of the structure analysis of a decagonal basic Ni-rich Al-Ni-Co quasicrystal. The refinement was conducted with only real space parameters. We used a decorated rhombic Penrose tiling as an initial structure for the refinement process. With the statistical approach we could derive the structure factor unrelated to the perpendicular space. This is a very convenient approach as it allows us to treat atomic positions as phase coefficients of the Fourier transform. Furthermore, the structure factor we used was derived in a strict; i.e. without any approximations, mathematical way.

We obtained $R = 12.3\%$ and the $wR = 6.2\%$ for 2767 reflections. 106 parameters were refined. The resulting structure has the exact chemical composition Al$_{70.7}$TM$_{29.3}$. The refined structure has the point density $0.0656$ Å$^{-3}$ and overall density $3.94$ g/cm$^3$, which is very close to experimental values.

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