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Atomic Structure of Decagonal Al-Cu-Rh Quasicrystal–Revisited: New Correction for Phonons

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Abstract: The standard approach applies the Gaussian distribution function to estimate atomic displacements due to thermal vibrations in periodic and aperiodic systems, which is used in a form of the Debye–Waller factor during the structure refinement. Acoustic phonons provide the largest contribution to the Gaussian correction although the character of other phonon modes remains relatively unclear. In this paper, we provide an alternative description of localized and dispersionless phonons based on an assumption of the harmonic displacement distribution function, which was recently proposed for model quasicrystals, and apply this approach for a decagonal Al-Cu-Rh quasicrystal that was previously studied by Kuczera et al. in 2012. We used the same X-ray diffraction data and the statistical method of structural analysis of the aperiodic systems. The correction function for phonons takes the form of a Bessel function instead of a conventional (Gaussian) Debye–Waller factor. This allowed us to achieve R-factor of 7.2% compared to 7.9% reported in the original paper. A significant improvement of the calculated atomic composition towards experimentally obtained and minor positional changes is also reported compared to the original paper. The results show the usefulness of investigating different corrective terms for diffraction data during a structure refinement.

Keywords: decagonal quasicrystals; phonons; statistical method

1. Introduction

Decagonal (*d*-) Al-Cu-Rh quasicrystals were originally investigated by Kuczera et al. and a comparative structural study with *d*-Al-Cu-Ir and *d*-Al-Cu-Co systems was performed [1]. That study showed the first refinement results of *d*-Al-Cu-{Rh,Ir} systems, whereas the *d*-Al-Cu-Co was previously refined using in-house X-ray diffraction data [2]. The refinement was conducted based on the Average Unit Cell (AUC) concept [3–5], which is a method that involves the modeling of the aperiodic systems (called the *statistical method* in the next parts of the paper), which is the main alternative to the multidimensional one. The same method is used in this paper. We focus on the novel approach to phonons, which is accessible within the statistical method. In reference [6], we theoretically speculated about possible benefits from replacing the standard Debye–Waller (D–W) factor with different functions, such as Bessel functions (ordinary or spherical). The standard D–W correction is a Gaussian exponent with a squared scattering vector k in the exponent [7]. The exponential correction function strongly affects the intensity of the large k peaks, which can be falsely miscalculated during refinement. In references [6,8], we showed the usefulness of Bessel-like functions (ordinary and spherical) as good correction functions for phonons, which suggests the crucial role of weak reflections in the refinement of quasicrystals. The goal of this paper is to show

how this new approach contributes to a better refinement result of the decagonal quasicrystal. The new theory of phonons in quasicrystals is not a subject of the present paper. The state-of-art hydrodynamic (or elasto-hydrodynamic) theory has been developed and successfully used in the field of quasicrystals for many years [9–11]. Our goal is to determine how a very simple assumption on harmonic atomic displacements from ideal positions, which leads to the Bessel-like corrective term for phonons, influences the refinement results of a real decagonal system. We chose *d*-Al-Cu-Rh system for a detailed study due to the high quality of the data available for this system. As reported in reference [1], the diffraction pattern of *d*-Al-Cu-Rh is free from the diffuse scattering, which means that it is likely that these refinement results are of the best quality. This is confirmed by the observation that *d*-Al-Cu-Rh system has the smallest substitutional disorder with no Al/Cu and Cu/Rh mixing present. *d*-Al-Cu-Rh is believed to be one of the best ordered quasicrystalline system.

2. Phonons in Quasicrystals: A Statistical Approach

Since the discovery of quasicrystals in 1982 [12], the problem of phonons (and complementary subject of phasons) was studied both theoretically and experimentally. The very first hydrodynamic theory of lattice dynamics appeared to be a most successful one so far [8–10]. Soon after the hydrodynamic theory was established, more detailed theoretical studies on phonons in quasicrystals were performed [13–15]. Since the very early stage, it was clear that phonons and phasons are complementary phenomena observed in aperiodic crystals and a strong coupling of the two occurs [14]. The elastic constant related to the phonon–phason coupling appeared to be rather small due to theoretical predictions based on hydrodynamic theory for icosahedral quasicrystals [16] and simulations performed with pair-potentials for decagonal systems [17] or double-well potentials for model Fibonacci chains [18]. The elasto-hydrodynamic model of phonons and phasons for decagonal quasicrystals was analytically derived in detail quite recently [11]. At the early stage of studies, it was believed that it was not possible to observe phonon–phason coupling in an experiment [19]. However, more recent results show that the phonon–phason coupling can be investigated experimentally [20]. It is yet very small and with a very good accuracy, it can be neglected in the majority of cases. Since the phonon–phason coupling is not strong, the consideration of phonons and phasons can be performed independently during a refinement process. Quasicrystals possess no translational symmetry. However, it is proved numerically and experimentally that we should expect long-wavelength propagation of phononic modes at least for the acoustic phonons. It was experimentally shown and confirmed by numerical calculations that for a (rather short) regime of ~0.3 Å^{-1}, we can observe a sharp acoustic branch in the phonon spectra with a linear dispersion relation for icosahedral [21–23] and decagonal quasicrystals [17,24]. We can assume that the long-wavelength acoustic phonons are the main contribution to the standard (exponential) D–W factor [25]. However, the same studies show that higher-energy phonons are not well separated in the dispersion curves and strong broadening is observed. At even high energies, in the range of optical (or optic-like) modes, rather dispersionless smeared modes can be measured [22,23]. Simulations confirmed that optical modes are localized and possess no clear dispersion relation – either in icosahedral [26], and decagonal system [17]. It is known that for quasicrystals, we observe essentially infinite number of gaps in excitation spectra within a pseudo-boundary zone. The higher-energy optical phonons are thus localized [25].

The diffraction pattern considered within the statistical approach is strongly related to the probability distribution function of atomic positions in the AUC [3–6]. For periodic crystals, the distributions are discrete and can be described as a sum of Dirac-delta functions. For quasicrystals, the distributions are continuous. For instance, in the case of the decagonal systems modelled by the Penrose tiling, which are scalable systems, the distributions are non-zero only along characteristic lines (see: τ^2-scaling in quasicrystals in [3,5]). Defects cause the perturbation of these distributions. The effects of the broadening of scaling lines along the [1,1] direction in the reduced {u,v} coordinates result in the phonon-like disorder. The defects that are observed as perturbations along the lines are phason-like and can be related to rearrangements of atoms (flips) in the system. A fully correct description of phonons is rather difficult, because it requires a full picture of modified distributions (which are difficult to model). The easiest (and

safest) assumption is to consider a Gaussian broadening of the scaling line, which is enough for strong reflections (up to 1% of the dynamical range of relative intensities in the diffraction pattern). The Gaussian approximation strongly diminishes the weak reflections (below 1% of the dynamical range). One of the possible solutions might be to not follow the Gaussian approximation approach to phonons and instead successfully describe all reflections in a broad dynamical range ($1-10^{-6}$ with respect to the strongest reflection). This is a subject of our paper. One possibility is to use Bessel functions, which are characteristic for harmonic phenomena. We propose a new approach, with the use of Bessel functions. In our approach, we do not consider thermal (or dynamic) effects in the systems leading to atomic vibrations, because it is beyond the modern theory of quasicrystals, but we rather determine the statistics of atomic displacements from their ideal positions. The "nature" of the displacement may be of temperature-related origin or other types of defects. The position of a single atom in the structure, which undergoes a harmonic interaction, can be defined by a sine function. The statistics of harmonic shifts of all atoms in the system that has been Fourier transformed can be used to create a Bessel function of the first kind and order 0 (this has been proven and largely described in our previous papers [6]). The derivation is based on simple physical assessments. Bragg peaks in the diffraction pattern contain the information about an average structure and the time-averaged atomic displacements. The influence of the atomic vibration on the diffraction phenomenon can be considered by collecting the statistics of atomic positions in time and representing this information as a spatial distribution of atomic positions. Therefore, the distribution of deviations from equilibrium can be used to calculate the corrective term in the structure factor. The use of Bessel correction function in the refinement process significantly improved results for weak reflections and did not worsen results obtained for strong reflections (see results of the refinement in this paper). For more details about Bessel-like correction in a statistical approach, see further parts of the present paper.

In our paper, we apply a Bessel-like approximation to the phononic corrective term, which is based on a simple assumption. Since optical phonon modes are dispersionless, we attribute Einstein model to the individual optic branch with a harmonic (sine-like) vibration around the equilibrium position and a given (single) frequency. The Fourier-transform of the harmonic displacement gives a Bessel-like term in the reciprocal space. For a broad energy-range of optical phonons, one should assume a linear combination of multiple Bessel functions (corresponding to different frequencies of optical phonons). For a simple case, we can only limit this to the single optical mode (of an average frequency). We find that this approximation is still more interesting than a standard D–W factor, which does not properly include optical modes of quasicrystals. The new way of treating phonons during a refinement process would be to combine a standard D–W factor, which includes a contribution of delocalized thermal vibrations (mostly acoustic modes), together with the Bessel-like term, which may be considered as a correction for all localized states (mostly optical modes) in quasicrystals. Although the hydrodynamic theory of lattice dynamics of quasicrystals is well-developed, there are still unanswered questions. The propagation of vibrational modes in quasicrystalline medium is not explained, since the Bloch theorem simply breaks this down into aperiodic systems. Some mathematically rigorous results, which were mostly obtained for 1D model systems, show that phononic eigenstates may have very different behavior (exponential decay, localized or critical points), which is even less clear for 2D and 3D quasicrystals [25,27]. New models of phonons for quasicrystals, perhaps beyond the hydrodynamic theory, is expected. In this paper, we make an attempt to apply a new Bessel-like correction for phonons to investigate a possible improvement of the refinement results for a real Al-Cu-Rh decagonal system.

3. *d*-Al-Cu-Rh: Experimental Details and Starting Model

For our study, we used the diffraction data collected by Kuczera et al. and published in a collective paper for Al-Cu-*Me*, *Me*={Co, Ir, Rh} [1]. All experimental details can be found there. Here, we only provide a basic overview of the sample and the experiment. For sample preparation, the arc melt technique was used. The starting element composition was chosen to be $Al_{64.5}Cu_{16.8}Rh_{18.7}$ according to the phase diagram presented in reference [28,29]. Compacts closed in Ta ampoules were melted, annealed in 1173 K for 2 weeks and finally, quenched in water. The exact chemical formula was

determined using scanning electron microscopy energy-dispersive X-ray spectroscopy (SEM/EDX) measurements to be $Al_{61.9(3)}Cu_{18.5(4)}Rh_{19.6(1)}$. The single crystal with an irregular shape and size of 30 × 30 × 30 μm was extracted from the sample and the X-ray data were collected using synchrotron radiation (wavelength 0.698 Å, angle step 0.1°). The experiment was performed at the SNBL line at the ESRF synchrotron in Grenoble, using KUMA KM6-CH diffractometer equipped with Titan CCD detector. The integration and processing of the data was done using CrysAlis Pro software. A total of 162,939 reflections and 2370 unique reflections were collected. The reconstruction of the reciprocal space enabled us to determine the centrosymmetric five-dimensional space group $P10_5/mmc$. No diffuse scattering was observed. The starting model for a refinement was determined based on the electron density maps phased using the SUPERFLIP software [30], which employed the charge flipping algorithm [31]. The rhombic Penrose tiling was derived in the quasiperiodic layers with rhomb edge-lengths of $a_r = 17.19$ Å (5-fold inflation was applied with respect to original Penrose rhombs in 5D description with a size of $a_{1-4} = \frac{1}{a^*} = 3.87$ Å, $a_r = \frac{2}{5}\frac{1}{a^*}\tau^5$). A total of 100 atomic positions in a projected thick rhomb (56 in the asymmetric part) and 64 atomic positions in a thin rhomb (36 in the asymmetric part), including edge positions, were derived from the electron density map in a starting decoration. Decagonal layers are ordered periodically along a perpendicular *c*-axis according to 10_5-screw symmetry with a period of 4.278 Å. Two atomic layers per period in *c*-direction rotated by 180° due to the screw axis were identified.

4. Structure Factor and Refinement Strategy

The structure factor was derived within the statistical method, which was previously applied in numerous refinements of decagonal systems [1,32–35] and structure models of icosahedral systems [36–38]. The basic concept of the method is the AUC, which is a probability distribution function $P(u)$ calculated as projections of atomic positions (called *u*) onto some periodic reference lattices. The range of *u* positions is limited to the period λ_k of the reference lattice. The probabilities $P(u)$ are 3D objects with a physical meaning, which play a role of a unit cell that is periodically repeated in real space. The AUC is the real-space counterpart of atomic surfaces, which is known in higher-dimensional crystallography. The two objects are linked by an oblique projection relation. Further details can be found in references [4,32]. Structure modeling within statistical method involves modeling of the shape and subdivision of the AUC. In the case of model quasilattice built with the rhombic Penrose tiling, the AUC takes the shape of 4 superimposed pentagons and can be divided into triangular regions associated with a given structural unit (thick or thin rhomb) in a given orientation. There are ten possible orientations of each individual structure unit. In our refinement procedure, we used the structure factor in the form known from previous works [1,33], which is namely:

$$F(\mathbf{k}) = D_{\text{phas}}(\mathbf{k}_{\text{perp}}) \sum_{t} \sum_{o=1}^{10} \left[F_t^o(\mathbf{k}) \sum_{j=1}^{N_t} p_j^t f_j^t D_j^t(\mathbf{k}) \exp\left(i\mathbf{k}\cdot\mathbf{r}_j^{t,o}\right) \right], \tag{1}$$

where $\mathbf{k}/\mathbf{k}_{\text{perp}}$ is the parallel/perpendicular component of the scattering vector, $F_t^o(\mathbf{k})$ is the Fourier transform of the triangular subregion of the AUC corresponding to a given rhomb ($t = \{\text{thick}, \text{thin}\}$) in a given orientation *o*, $\mathbf{r}_j^{t,o}$ is the position of an atom *j* in a given rhomb *t* for orientation *o*, p_j^t is the fraction of an atom *j* inside a rhomb *t*, N_t is the number of atoms decorating a rhomb *t* and f_j^t is the atomic form factor calculated as an average of individual atomic form factors f^{el} for elements $el = \{\text{Al}, \text{Cu}, \text{Rh}\}$ weighted with their occupation probabilities (concentrations) $p_{j,t}^{el}$ as follows:

$$f_j^t = p_{j,t}^{Al} f^{Al} + p_{j,t}^{Cu} f^{Cu} + p_{j,t}^{Rh} f^{Rh}, \tag{2}$$

with $p^{\text{Al}}_{j,t} + p^{\text{Cu}}_{j,t} + p^{\text{Rh}}_{j,t} = 1$. Two correction functions appear in the structure factor formula. The phasonic D–W factor (phasonic atomic displacement factor) $D_{\text{phas}}(\mathbf{k}_{\text{perp}})$ was in this paper calculated in a standard way for decagonal quasicrystals:

$$D_{\text{phas}}(\mathbf{k}_{\text{perp}}) = \exp\left(-\frac{1}{16\pi^2}\left(k_{\text{perp},x}^2 + k_{\text{perp},y}^2\right)b_{\text{phas}}\right) \tag{3}$$

with phasonic atomic displacement parameter (ADP) b_{phas} used as a single parameter to fit. A significant novelty of this paper is the usage of non-standard corrective terms for phonons with a Bessel function. Correctness and usefulness of such approach was discussed in [6,36,39]. The exponential D–W function was replaced by a novel Bessel phononic displacement function in a form:

$$D^t_j(\mathbf{k}) = J_0\left(\frac{1}{8\pi}\left(d_{xy}k_{xy} + d_z k_z\right)\right), \tag{4}$$

where J_0 is the Bessel function of the first kind of order 0, k_{xy}/k_z are lengths of components of the parallel reciprocal space function in the quasiperiodic plane and in the periodic direction, respectively and d_{xy}/d_z are the corresponding ADPs. The square mean displacement $u^2_{xy(z)}$ of atoms from the equilibrium positions is related to the ADPs and can be calculated as follows:

$$\langle u^2_{xy(z)} \rangle = \frac{d_{xy(z)}^2}{128\pi^2} \tag{5}$$

The origin of the Bessel function correction type in quasicrystals is justified by the observation made within the statistical method of a structural investigation. If we assume that atomic shifts from equilibrium positions are subject to harmonic (sine-based) instead of Gaussian distributions, the phononic effect on intensities' envelope shape is given by a Bessel function instead of a Gaussian (see detailed discussion under Figure 1). In Figure 1, this effect is shown for model 1D quasicrystal—Fibonacci chain.


(a)　　　　　　　　　　　　　　　　　　　　　　　(b)
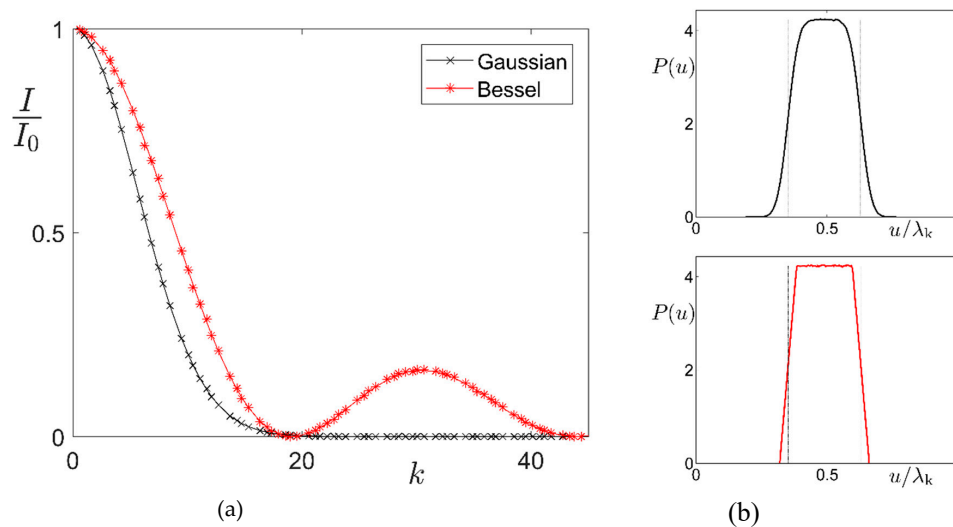
Figure 1. (**a**) Envelopes of the diffraction peaks' intensities for the Fibonacci chain (one-dimensional quasicrystal) with phonons, I, calculated vs. intensities for perfect Fibonacci chain without phonons, I_0. This is obtained by two different shapes of atomic distributions around ideal positions: Gaussian (black crosses) and Bessel function (red stars). Generally, the set of peaks is infinitely dense and its arrangement is aperiodic. For clarity, only peaks with limited indices and intensities are shown. Intensities are calculated within the statistical method as the squares of the Fourier transform of the corresponding distribution function $P(u)$. (**b**) The corresponding probability distributions AUC are given by Gaussian (black) and harmonic (red) distributions. For ideal positions (no phonons), the uniform probability distribution $P(u)$ is observed (marked with dashed lines).

The refinement was performed using a self-written software implemented with the Matlab programming tool. The interior-point algorithm provided by *fmincon* function was used as the minimization algorithm against the intensities of the experimental peaks. A total of 2092 unique reflections with amplitudes $|F| > 1\sigma(|F|)$ were used for the refinement. The R-factor was an optimized function with constraints put on a composition and a material density. Furthermore, lower and upper bounds were set for parameters to range in a physically meaningful regime. The refinement was carried out in steps. The final parameters for atomic positions, phasonic ADP and other from the solution by Kuczera et al. were used as starting parameters in our refinement. These parameters were slightly optimized. The only parameters to fit from the scratch were ADPs, which were now defined for a Bessel function-based D–W factor. Having obtained the initial values of ADPs, the chemical composition within the experimental constraints was refined. The third step was the refinement of atomic positions. The *z*-component of an atomic position was assigned to be 1/4 or 3/4 of the period along *c*-axis, which was based on the distance of an atom from a respective atomic layer within 0.15 Å. Finally, all parameters, including phasonic D–W factor and extinction, were refined in the last step.

5. Refinement Results and Structure

The log-log plot of calculated vs. observed diffraction amplitudes ($|F_{calc}| / |F_{obs}|$) is presented in Figure 2 for 2092 peaks with dynamical range of 3 orders of magnitude. Characteristic bias is present in the low-intensities regime, which is typical behavior that is known for quasicrystals and complex metallic alloys. To our knowledge, there are at least two possible reasons for this phenomenon, which are namely (*i*) incorrect phasonic correction function and/or (*ii*) multiple scattering effect occurring in the diffraction experiment. Discussion on the influence of possible scenario (*i*) is explained in detail in references [5,6,40]. The standard exponential phasonic D–W factor with $\mathbf{k}_{perp}$ vector in the exponent (see formula (3)) appears to artificially lower the intensities of reflections with large-$\mathbf{k}_{perp}$ component, which are small by definition for quasicrystals. The intensities of weak reflections become biased and even more decreased. The influence of multiple scattering in quasicrystals was recently numerically investigated [41], but there is still a lack of experimental evidence. After multiple scatters, the reflected X-ray beam is weakened and causes decrease of measured intensities [42]. Contrary to exponential phasonic D–W, this effect affects all reflections, but there is a majority of weak ones in quasicrystals, which may be the reason of an appearance of the bias in the low-reflection regime only. The two possible scenarios are also of further research interest to authors of the present paper. In Table S1 in Supplementary Materials, all calculated and measured diffraction intensities together with extinction parameters are listed compared to 6 components of a scattering vector.
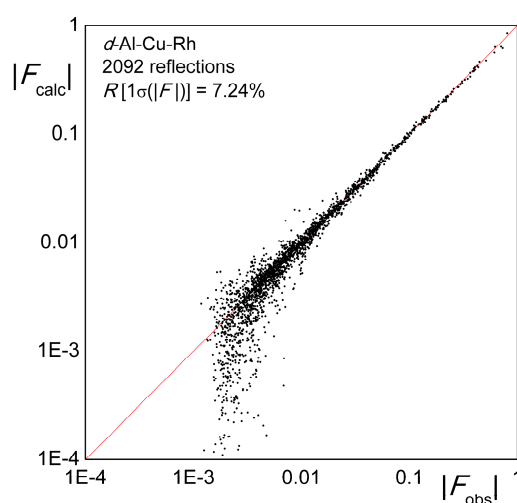
Figure 2. Calculated vs. measured amplitudes of 2092 unique reflections normalized to the strongest one. A typical bias is observed for small amplitudes <0.01.

The refined structure is actually identical with the one reported in reference [1] in terms of atomic positions. However, the refined composition is $Al_{62.2}Cu_{17.9}Rh_{19.9}$, which differs from the previous results for the experimental composition. Small discrepancies appear in occupancy parameters. The full list of atomic positions, occupancy parameters, phononic and phasonic ADPs and fractions in the units are given in Table S2 in Supplementary Materials. The overall phasonic ADP is $b_{phas} = 1.23$ Å^2, which is slightly higher than previously obtained. The total number of parameters to fit was 344 and the parameter-to-reflection ratio was 1:6.4. Different sections and projections of the unit rhombs of *d*-Al-Cu-Rh are shown in Figure 3. Only positional (split or partially occupied positions) disorder is present in the refined structure with no chemical one (mixed positions). As reported in reference [1], *d*-Al-Cu-Rh is one of the best ordered decagonal phases. The edge-lengths of the refined unit rhombs is 17.19 Å and the period along *c*-axis is 4.279 Å. Atomic layers are separated by a distance of ~2.19 Å and rotated by π due to the screw axis 10_5. Furthermore, due to the 5-dimensional space group $P10_5/mmc$, a mirror plane is present along the long diagonal of the thick rhomb and the short diagonal of the thin rhomb while 2 mirror planes are perpendicular to 10_5 screw axis along *c*-direction. For this reason, the split positions of atoms shifted off the $z = 1/4$ and $z = 3/4$ planes appear along the periodic direction.

(a)   (b)
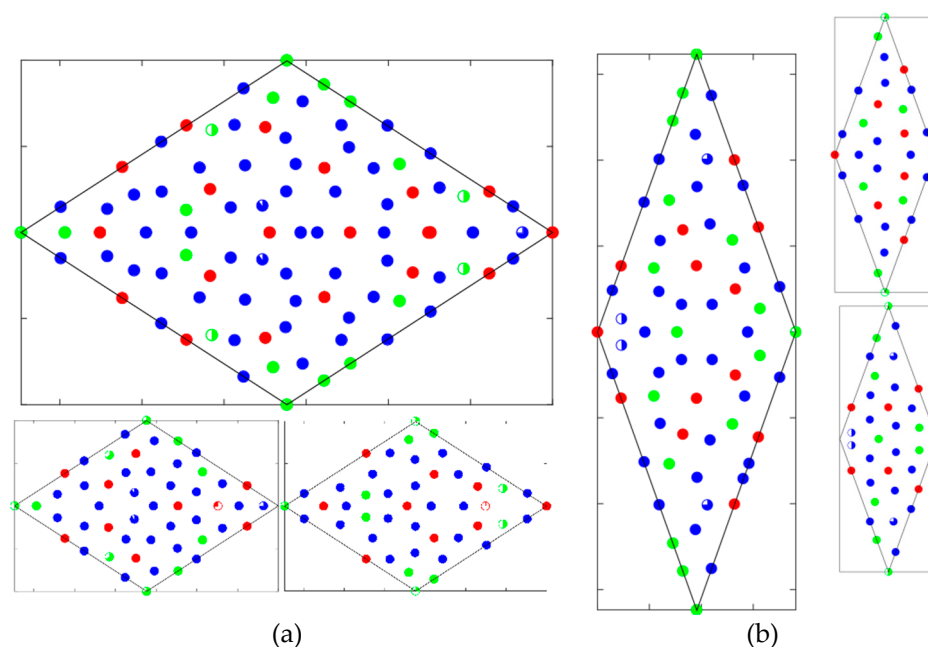
Figure 3. Decorations of structure units in the refined structure: (**a**) thick rhomb and (**b**) thin rhomb. Pairs of smaller rhombs represent decoration of unit tiles in different aperiodic planes along *z*-axis. Projections of decorated rhombs along *z*-axis are shown as large rhombs. Al atoms are marked with blue, Cu atoms with green and Rh atoms in red.

6. Summary and Outlook

The new repeated refinement of decagonal Al-Cu-Rh quasicrystals was performed with previously collected X-ray diffraction data and starting model derived by Kuczera et al. in 2012. A completely new approach to phonons was presented in this paper, where the usual Gaussian correction function for phonons was replaced by the spherical Bessel function of order 0. A physical justification for the new approach to phonons is based on a different statistical distribution of atomic shifts from ideal positions, which is a harmonic (sine-like) distribution, in contrast to Gaussian distribution for the classical approach. This new Debye–Waller function only introduced two parameters to fit per reflection. The same number of parameters is usually fitted in the case of a decagonal quasicrystal using a standard exponential Debye–Waller function. A significant role of the new phononic correction function appears most profoundly for weak reflections with large **k**-component of the scattering

vector (see Figure 1). Weak reflections, which are a majority in the diffraction pattern of quasicrystals, are additionally weakened by a fast decreasing tail of a Gaussian function, whereas oscillations of a Bessel function enhance the significance of weak reflections in the phenomenon of thermal vibrations. An improvement in the refinement result was achieved by decreasing R-factor from 7.9% (using the original refinement from reference [1]) to 7.2%.

The collected data for *d*-Al-Cu-Rh are of a high quality and can be used in further studies of phasons in quasicrystals. Our future efforts will be focused in explaining the typical bias in a log-log plot of refined and measured diffraction amplitudes. The two possible scenarios (new approach to phasons and multiple scattering effect, as discussed in chapter 4) will be checked for *d*-Al-Cu-Rh, which will hopefully further improve the refinement results and decrease in R-factor value. Furthermore, further development of the new approach to phonons is expected.

The refined atomic decoration of Penrose rhomb exhibits some split and partially occupied positions. This is probably due to the insufficient accuracy of the structural model used in the refinement. Based on this observation, another future study is planned. The limitations of rhombic (or pentagonal or kite-dart) Penrose tiling can be investigated and the Generalized Penrose Tiling [43] can be used. Generalized Penrose tilings offer the possibility of simultaneous refinement of a family of different models, offering new decoration schemes, by introducing only one extra parameter to fit (a shift of atomic surfaces along perpendicular *z*-direction).

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4352/9/2/78/s1, Table S1. Diffraction pattern of *d*-Al-Cu-Rh. List of 6 components of the scattering vector, parallel (k_x, k_y, k_z), and perpendicular (k_x^{perp}, k_y^{perp}, k_z^{perp}), measured amplitudes ($|F_{\mathrm{obs}}|$), their uncertainties ($u(|F_{\mathrm{obs}}|)$), calculated amplitudes ($|F_{\mathrm{calc}}|$), and extinction parameters (ext). Table S2. Atomic structure of *d*-Al-Cu-Rh. List of atomic positions (*x*,*y*,*z*) concentrations of elements (p_{Al}, p_{Cu}, p_{Rh}), site occupation (sof), ADPs (d_{xy}, d_{zz}), and atomic fraction in unit rhomb (fraction). The last row shows the phasonic ADP (b_{phas}).

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Conflicts of Interest: The authors declare no competing interests.

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