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STRUCTURAL DISORDER IN QUASICRYSTALS

One of the challenges of modern crystallography of complex systems (complex metallic alloys, proteins, aperiodic crystals and quasicrystals) is to properly describe the disorder in these systems and discuss correctly the refinement results in terms of the structural disorder. In this paper we briefly discuss a new approach to phasons and phonons in quasicrystals and focus on the new theory of phonons in these materials. A newly derived correction factor for phonons in the form of the Bessel function is the approximated way of describing optic modes in the phonon spectra of quasicrystals. It is applied to a real decagonal quasicrystal in the Al-Cu-Rh system with 56/38 atoms per thick/thin structural unit, based on 2092 unique reflections selected from the collected diffraction data, significantly improving the refinement results. The final *R*-factor value is 7.24%, which is over 0.5% better result comparing to originally reported. We believe our work will open a broader discussion on the disorder in quasicrystals (and other aperiodic systems) and motivate to develop new approaches to treat the diffraction data influenced by different types of disorder in the new way.

Keywords: quasicrystals, structural disorder, phonons, phasons, structure factor

1. Introduction

Quasicrystals are aperiodic structures which undergo two main types of atomic disorder: (*i*) atomic oscillations around equilibrium positions (phonons), and (*ii*) flips of atoms between equivalent positions (phasons). The latter is a characteristic of quasicrystals [1]. Both phenomena influence the diffraction pattern by reducing the intensities and broadening of the peak profiles. In all modern refinements of quasicrystals, likewise of crystals, the correction for all structural disorder is made by multiplicative corrective factors, namely the Debye-Waller factor (D-W) with exponential form $\exp(-k^2\sigma^2)$ (phonons) or $\exp(-k_\perp{}^2\sigma_\perp{}^2)$ (phasons), where $k/k_\perp$ is the parallel-/perpendicular-space component of the reciprocal space scattering vector. We show that the exponential multiplicative factor fails in the context of phasons and it even worsens the refinement result by introducing a characteristic bias in the plot of calculated *vs.* fitted intensities [2].

One of the big challenges in crystallography of quasicrystals is to properly treat weak reflections in the refinement process. We know, that quasiperiodic diffraction pattern consists of infinitely dense peaks assemble, of which majority is of very small intensities. On the other hand, all modern refinement results suffer from the underestimation of the intensity in the weak-reflections regime in the log-log plot of calculated *vs.* measured intensity [3,4]. In our previous works we suggested that the reason for the characteristic bias in the refinement results may be the improper treatment of the phasonic correction to the diffraction data together with the effect of the multiple scattering. Both phenomena, and especially the latter, are not satisfactorily described with a physically justified theory. In our previous work we showed, that currently used Debye-Waller factor of exponential form is justified and valid for random tiling type structure only [5]. We introduced a novel approach to phasons (and phonons) in quasicrystals based on the statistical method of structural investigation of crystals [6,7]. The very first approach to include multiple scattering effect in the refinement of real quasiperiodic crystal was done in our group very recently [8].

2. Phonons in quasicrystals

In this paper we discuss the new approach to phonons in quasicrystals with the use of the statistical analysis of aperiodic systems. As we know, phonons are caused by thermal vibrations of atoms around ideal positions in the crystal lattice. The quasiperiodic systems possess, however, no periodic lattice, and the propagation of phononic vibrations through the system cannot be compared directly to periodic crystals. Many results published

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in literature confirm the strong evidence (both experimental and theoretical) of sharp acoustic phonon branch [9-11]. Since the Bravais lattice does not exists in the case of quasicrystals, the Brillouin zone for these materials is rather considered as infinite (or numerous) assemble of narrow zones, so the phonon branch is fragmented. However, it still resembles very well the linear trend, as it is exactly in the case of periodic crystals. Linear dispersion relation leads to the exponential Debye-Waller factor, as theory of condensed matter physics predicts. The detailed description of the optical modes is, however, still not available for quasicrystals. We know from experiments and calculations, that the modes are rather localized and dispersionless [12,13]. The new approach to phonons in quasicrystals appears to be expected.

2.1. Theory of phonons within statistical analysis

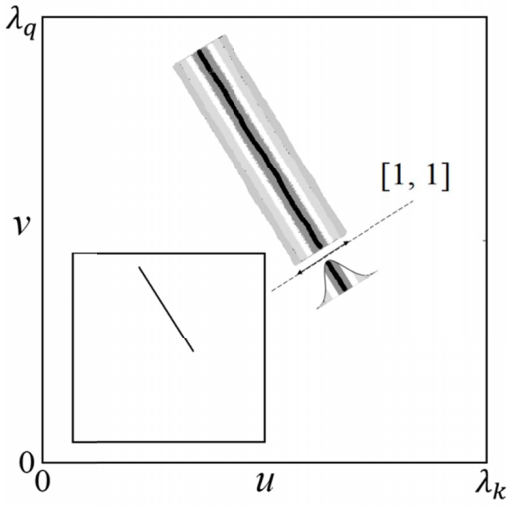
The statistical distribution is, next to the higher-dimensional approach, the most successful method of describing structure and diffraction pattern of aperiodic crystals, including quasicrystals [14-17]. Its basic concept is the introduction of the statistical probability distribution P of atomic positions calculated against some reference lattices, which plays a role similar to atomic surfaces (also called occupation/acceptance domains or windows) in the higher-dimensional approach. Because quasicrystals are two-length-scale systems, we introduce two reference lattices, and get new positions u,v calculated as distances of real atomic positions with respect to the nearest nodes of the lattices. After introducing the scaling relation (which for known quasicrystals is given by the golden mean $\tau \approx 1.618$), the positions u and v are not independent, but follow the linear dependence: $v = -\tau^2 u$. This relation is called TAU2-scaling. The distribution $P(u,v)$ is dense and uniform and depends on the dimensionality, chosen reference lattices, and underlying quasilattice. It is an object constructed in the physical space and, repeated periodically, fully describes the structure. For this reason, we call it an Average Unit Cell (AUC).

The structure modeling of quasicrystals is based on the modeling of the AUC – Fourier transform of the AUC gives a structure factor, and its squared modulus contributes to the diffraction intensity. The shape of the AUC for the Penrose tiling is given by 4 pentagons (two smaller and two bigger, with inversion) [18]. For a simple 1D model of quasicrystals (Fibonacci chain) the AUC is a flat distribution of a given (finite) height and width (see Figure 1(right)) [19]. For periodic crystals, the distribution becomes sum of Dirac-delta functions. For further details on the AUC approach to structure modeling see [6,7,20-22].

We explain the influence of phonons on the structural analysis of quasicrystals on the example of 1D Fibonacci chain (for simplicity). If the atomic vibration around equilibrium position have a Gaussian distribution (positional displacement undergoes a normal distribution), the linear dependence $v(u)$ is smeared along [1,1] direction in (u,v)-space (see Figure 1(left)). The shape of the AUC is also influenced by the distribution of atomic displacements and gets a Gaussian shape too. Fourier-transformed AUC leads to the standard exponential correction function for phonons, known as Debye-Waller factor (or atomic displacement parameter, ADP). The statistical method, however, gives a full freedom in considering different distributions, G, of atoms undergoing thermal fluctuations. Let u_p, v_p be the displacements of atoms from the equilibrium positions (measured against reference lattices and undergoing the distribution G). New coordinates in the AUC are: $u^{new} = u + u_p$, $v^{new} = v + v_p$. The new probability distribution $H(u_{new}, v_{new})$ is within the statistical approach a convolution of the original distribution $P(u,v)$. and distribution $G(u_p, v_p)$ (pairs u, u_p and v, v_p are independent). Fourier transform leads to the following structure factor formula:

$$F(k) = \int_0^{\lambda_k}\int_0^{\lambda_q} P(u,\ v)\, e^{i\left(h_1 k_0 u + h_2 q_0 v\right)} \mathrm{d}u\mathrm{d}v \int_0^{\lambda_k} G\left(u_p\right) e^{i\left(h_1 k_0 u_p + h_2 q_0 u_p\right)} \mathrm{d}u_p \qquad (1)$$

where k_0, q_0 are reciprocal space vecto, for which the reference lattices are constructed (lattice constants are $\lambda_1 = 2\pi/k_0$ and $\lambda_2 = 2\pi/q_0$), and h_1, h_2 – integer indices.



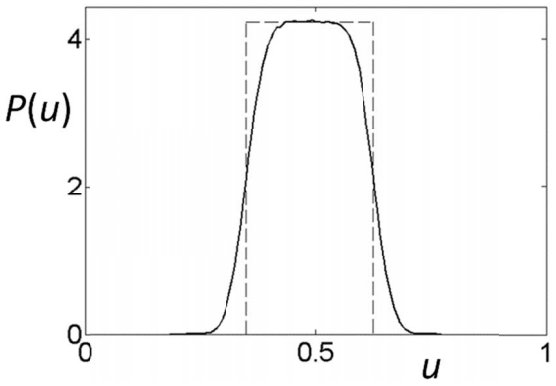


Fig. 1. (left) TAU2-scaling for the Fibonacci chain: linear dependence $v = -\tau^2 u$ in the case of ideal structure (see inset) gets smeared along [1,1] direction in the (u,v)-space. Gaussian distribution of atomic displacements from ideal positions applied. (right) The AUC for ideal Fibonacci chain (dashed line) gets smeared according to a Gaussian function if the phonons occur in the system (solid line)

Very important conclusions come from the formula (1): (*i*) the correction for phonons is a multiplicative factor to the structure factor of an ideal structure (like the Debye-Waller factor in standard analysis); (*ii*) no assumptions on the distribution G have been made in the course of deriving the above formula. It is then a general formula. For further details see [2]

The very interesting case is when we consider a harmonic distribution $G(u_p, v_p)$ of atomic displacements from ideal positions (given by the sine function). It is a very simplistic model of atomic vibrations under forces of the harmonic-oscillator-like character, which lead to positions u_p, v_p given by the sine function of time. We can now refer to the experimental observations, that optical modes of phonons in quasicrystals are rather localized (with a single given frequency), which is a parameter of a sine function in G. With such a choice, a Fourier transform of G gives Bessel functions of the first kind, J.

3. New phononic correction for decagonal Al-Cu-Rh quasicrystal

3.1. Sample and measurements

In this section we present the application of the new phononic correction for a decagonal quasicrystal in the system Al-Cu-Rh. We use the diffraction data collected previously by Kuczera et al. [4]. Here, we report only basic information on the sample preparation and diffraction experiment conditions. Decagonal quasicrystal Al-Cu-Rh is one of the best ordered decagonal system reported in literature [4,23]. First stable samples were obtained by Tsai et al. in 1989 [24], but only in 2012 first structure investigation with X-ray diffraction was done by Kuczera et al. Single crystals were prepared by arc melting technique with 2-week annealing period and quenching in water, afterwards. Samples of size 30×30×30 μm were selected and the chemical composition was investigated by EDX technique to: $Al_{61.9(3)}Cu_{18.5(4)}Rh_{19.6(1)}$. The diffraction experiment was performed using synchrotron radiation at ESRF Grenoble with a single crystal diffractometer KUMA KM6-CH equipped with CCD detector Titan, in room temperature. XRD data contained in total 162,939 reflections (2370 unique, of which 2092 were used for the refinement). The Laue symmetry was found to be $P10_5/mmc$ with screw axis along the periodic direction. For further details see [4].

3.2. Starting model and structure factor

Starting model was constructed based on the electron density map retrieved from the XRD data with the use of charge flipping algorithm implemented in Superflip program [25]. Edge-length of the Penrose tiles was a = 17.19 Å, and the period along c axis was 4.278 Å. Two atomic layers are arranged along periodic axis with an inversion symmetry due to 10_5-screw symmetry. The assymetric parts of thick/thin rhombuses were decorated with 56/38 atoms and the decoration was taken from the final decoration of the Kuczera's model (see Fig. 2).

The structure factor of decagonal quasicrystal with arbitrary decoration using the Penrose tiling as a quasilattice within the statistical method was first derived in [18]. We modified slightly

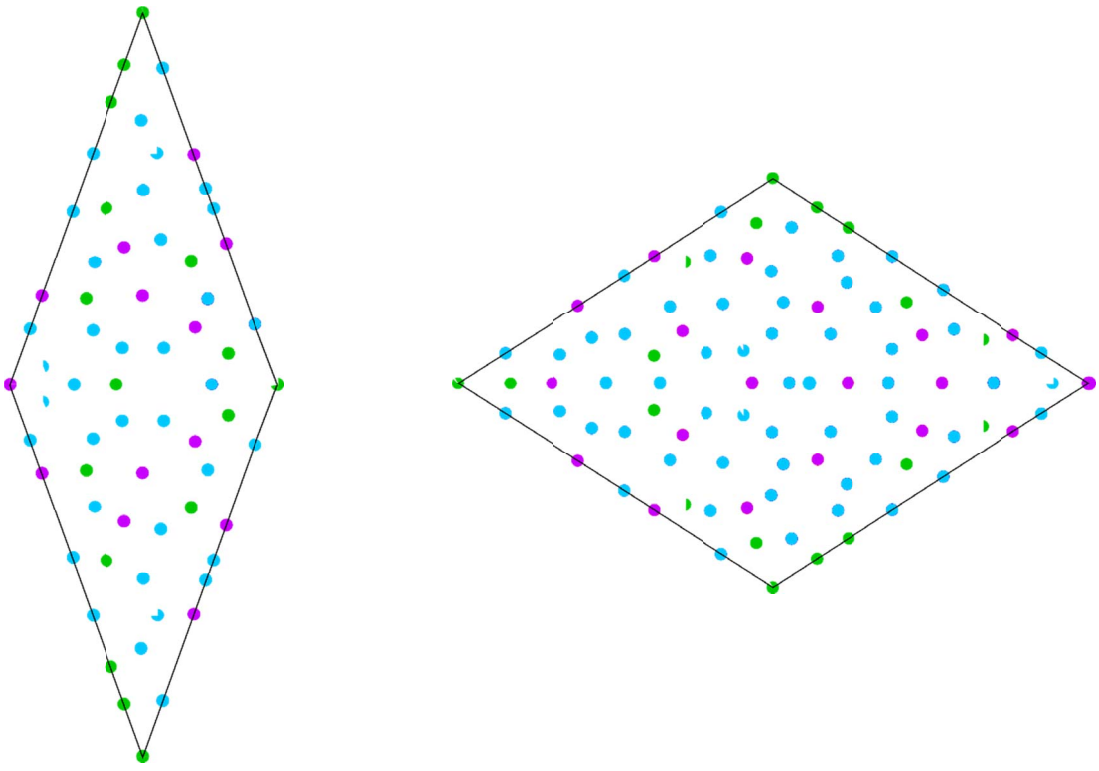


Fig. 2. Starting decoration of thin (left) and thick (right) Penrose rhombuses with Al (light-blue), Cu (green) and Rh (violet) atoms. Partial occupancies marked with incomplete circles

the structure factor to include new correction for phonons. In our refinement program we used the following phononic correction given by the Bessel function of the first kind:

$$D_j^t(\boldsymbol{k}) = J_0\left(\frac{1}{8\pi}\left(d_{xy}k_{xy} + d_z k_z\right)\right) \quad (2)$$

where 2 parameters to fit (defined for each atom) are related to atomic displacements as follows: $u_{xy(z)}^2 = \frac{d_{xy(z)}^2}{128\pi^2}$. The phasonic Debye-Waller factor was used in a standard exponential form.

3.3. Refinement results

The refinement procedure was conducted using the interior-point-algorithm with *R*-factor as a convergence parameter implemented in Matlab code as the minimization algorithm. The *R*-factor was calculated for 1σ reflections only. In the reference paper (original result by Kuczera et al., obtained with standard Debye-Waller factor for phonons) the refinement results of $R = 7.9\%$ was achieved. After using the Bessel-like correction for phonons our refinement converged with $R = 7.24\%$. The improvement of the results is quite significant (of about 9% of original *R*), which might suggest the successful use of the new correction for phonons developed within the statistical method. Final atomic structure does not change much and is essentially the same as the starting model. Also, ADPs for phasons is comparable.

4. Summary

In this paper we discussed the problem of disorder in quasicrystals, with focus on phasons and, in more details, phonons. We suggested, that the new theory of phonons and phasons is expected in the field of quasicrystals and proposed a new approach, based on the statistical method of structural analysis of aperiodic crystals. Due to the lack of translational symmetry, we cannot build the theory of phonons in quasicrystals in the same manner as in the case of periodic crystals. Despite the experimental and theoretical evidence of rather sharp acoustic branch, the physics of optical modes remains an open question. We suggest to apply the Einstein approximation of dispersionless phonons in the optical regime and the distribution of atoms around equilibrium positions given by the harmonic function. This leads to Bessel-like correction function for phonons in the reciprocal space. The new correction applied to real decagonal system of Al-Cu-Rh significantly improves the refinement result. It must be stressed, that in our refinement procedure we used the Bessel correction exclusively. The correction function in the form of standard Debye-Waller factor is, however, expected due to supposed acoustic phonon branch in this decagonal system. Not taking into account the exponential phononic correction still lead to a better fit.

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