ATOMIC-SCALE CHEMICAL ORDERING OF Co AND Ni IN CRYSTALLINE APPROXIMANT RELATED TO Al-Co-Ni DECAGONAL QUASICRYSTAL

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It is well-known that several structural modifications of decagonal quasicrystals (DQCs) exist in Al-Co-Ni alloys with a wide compositional ratio of Co/Ni [1]. These phases are stabilized by chemical ordering between Co and Ni, however the investigation of the ordering has never been performed because of containing neighbor’s elements Co (Z = 27) and Ni (Z = 28). We visualized atomic-scale element maps for a PD3c phase (orthorhombic unit cell with lattice parameters $a = 5.2$ nm, $b = 0.4$ nm and $c = 3.7$ nm) [2], which is an important approximant for understanding the structures of ordered Al-Co-Ni DQCs [3], in an annealed Al$_{71.5}$Co$_{16}$Ni$_{12.5}$ alloy by spherical aberration (Cs)-corrected STEM and atomic-scale EDS by using a Cs-corrected electron microscope (JEM-ARM200F) in order to elucidate the nature of the chemical ordering [4].

Figure 1 shows an HAADF-STEM image (a) and EDS maps of Co and Ni elements (b: green, c: red). The 1.2 nm clusters are enclosed by circles in Figs. 1(a) and 1(d). A separation of the Co- and Ni-rich areas is clearly exhibited in the overlapped maps (Fig. 1(d)) with Co and Ni. As shown in Figs. 1(a) and 1(d), the TM atoms in the 1.2 nm cluster are Co atoms (green), on the other hand, MSs located in gaps between the 1.2 nm clusters are occupied by Ni atoms (red).

On the basis of the present EDS mappings, it can be concluded that the chemical ordering of Co and Ni occurs between the 1.2 nm clusters and pentagonal MSs. It is reasonable to consider that a change of the area ratio of the Co-rich 1.2 nm clusters to Ni-rich pentagonal MSs causes a series of DQCs with different Ni/Co ratios.


Figure 1. a) HAADF-STEM image and atomic-scale EDS maps of Co (green, b) and Ni (red, c) for the same area. (d) overlapped maps with (b) and (c).
MULTIPLE DIFFRACTION IN AN ICOSAHEDRAL Al-Cu-Ru QUASICRYSTAL: X-RAY EXPERIMENT AND SIMULATION

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Most intensity of reflections in X-ray diffraction is affected in varying degree by multiple diffraction (MD) effects. When three or more reciprocal lattice points make contact with Ewald sphere, the reflections satisfying the diffraction condition are simultaneously excited. As the result of interaction between reflected beams, modified intensities of the reflections are observed. MD effects in quasicrystals (QCs) are thought to be more serious than ordinary crystals since they are characterized by a dense set of reciprocal lattice points. Indeed, a preliminary experiment on an icosahedral Al-Cu-Fe QC has shown that the intensity of weak reflections can be significantly changed by MD effects [1]. In order to find a way to correct such an experimental artefact, a complete understanding of MD effects in QCs is necessary.

Here we report our study on MD effects in an icosahedral Al-Cu-Ru QC. A flux grown QC with spherical shape (255 μm in diameter, Al$_{67.0}$Cu$_{18.8}$Ru$_{14.2}$, $a_{\text{ico}}$ = 9.076 Å) was used as a specimen. Measurements were made on the Enraf-Nonius CAD-4 diffractometer with graphite (002) monochromatized MoK$_\alpha$ radiation at room temperature. For several reflections along different symmetry axes, the $\psi$-scan was made in steps of 0.05°; the intensity at each $\psi$ position being determined from $\omega$–2$\theta$ scan. In order to interpret observations, we also developed a computer code for $\psi$-scan based on kinematical diffraction theories [2, 3]. Fig. 1 shows the $\psi$-scan pattern of 331-113 reflection along a 3-fold axis. Although the positions of most of MD peaks can be explained with the assumption that the QC has icosahedral symmetry, the variation of the intensity shows no 3-fold symmetry. This seemingly strange observation can be explained by anisotropy of mosaic spread in the flux grown QC. It is demonstrated that $\psi$-scan pattern is sensitive to the symmetry change of QC structure as in ordinary crystals.


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Since the availability of single grain quasicrystals (QCs), much research has been done on deposition of elements/molecules onto these surfaces [1]. This research has predominantly been related to how the adsorbates will arrange themselves according to the structure onto which they are being adsorbed, observed using STM. The QC Ag-In-Yb is one such sample in which recent work of this manner has been carried out [2-5], whereas previous work has been with Al-based QCs. It is considered that icosahedral (i-) Ag-In-Yb is comprised of Tsai-type clusters [6]. These clusters are interlocking shells of the constituent elements, ending in a rhombic triacontahedral (RTH) cluster. Due to the minimisation of surface energies the Ag-In-Yb QC is preferentially cut through the cluster centre. This provides particular “motifs” to be presented at the surface. It is at these motifs in which adsorbates are observed to preferentially adsorb.

A continuation of this observation leads to the hypothesis that any successive deposited elements will act to recreate the clusters that have been terminated. This has been recently shown on i-Ag-In-Yb in a display of a single element 3-dimensional Pb QC (whereas previous research demonstrates 2D thin films) [7]. The research carried out was on the 5-fold surface in order to reconstitute this structure as single element. In order to more comprehensively complete the research, the same is attempted on the 3-fold surface of the same i-Ag-In-Yb QC.

Data so far suggests that the Pb adsorbs according to the 3-fold symmetry of the substrate. Further deposition leads to growth of tetragonal Pb islands with approximately 1nm base edges (as seen in Fig. 1), in preference to completion of the previous monolayer.


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Figure 1. Growth of Tetragonal Pb Islands on i-Ag-In-Yb, 60 nm × 60 nm.
A NEW TYPE SUPERSTRUCTURE IN THE Al\textsubscript{11}TM\textsubscript{4}(TM = Ir, Rh) 1/0 QUASICRYSTALLINE APPROXIMANTS

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The Al\textsubscript{11}TM\textsubscript{4}(TM=Ir, Rh) compounds are binary 1/0 quasicrystalline approximants for Al-TM quasicrystals. The structure is a primitive cubic lattice with the space group P2\textsubscript{3} or Pm\textsubscript{3} (the lattice constant $a = 0.7674$ and 0.76692 nm, respectively) \cite{1}. Figure 1 shows the schematically illustration of the Al\textsubscript{11}TM\textsubscript{4} compounds. The unit cell contains “pseudo-Mackay” icosahedral cluster and there is a TM atom in centre of the TM icosahedron. But that possesses disordered Al site inside of the TM icosahedron. On the other hand, the ternary Al-Cu-TM 1/0 approximants possess the FCC lattice with the lattice constant $a = 1.5$ nm due to the ordered Cu site inside of the TM icosahedron. However, we observed very weak superlattice reflections in the selected area electron diffraction patterns for binary Al\textsubscript{11}Ir\textsubscript{4} \cite{2}. And Mihalkoviè reported the superstructure for Al\textsubscript{11}Ir\textsubscript{4} compounds by theoretical calculation. In this work, we investigated the superstructure and the composition dependence of the Al\textsubscript{11}Ir\textsubscript{4} and Al\textsubscript{11}Rh\textsubscript{4} by the powder X-ray diffraction method and transmission electron microscopy (TEM) study.

Al\textsubscript{11}TM\textsubscript{4} with composition ranging from 70 to 75 % Al were prepared by arc melting under an argon atmosphere. And the samples were annealed at 1373K for about 72 hours in the quartz tube under the argon atmosphere, followed by water quenched. Powder X-ray diffraction experiments were carried out using Cu K\textalpha to examine the phase constitution. Additionally, TEM study were performed by JEOL 2010F or TKP2 operating at 200kV. The samples for TEM were crushed by agate mortar and dispersed on micro-grid mesh.

Figure 2 shows selected area diffraction patterns of Al\textsubscript{72.5}Rh\textsubscript{27.5} and Al\textsubscript{72.5}Ir\textsubscript{27.5} taken along [011] and [111] direction. We observed the superlattice reflections at $h/2\ k/2\ l/2$ for Al\textsubscript{72.5}Ir\textsubscript{27.5} and Al\textsubscript{72.5}Rh\textsubscript{27.5}. In the case of [111] direction of Al\textsubscript{72.5}Ir\textsubscript{27.5}, the superlattice reflections appeared at the point to break the 3-fold symmetry. It shown that the type of superstructure of Al\textsubscript{72.5}Rh\textsubscript{27.5} is different from that of Al\textsubscript{72.5}Ir\textsubscript{27.5}. Additionally, XRD superlattice peaks disappeared in the poorer Al compositions for Al-Rh system. The composition dependence on the superstructure suggests that the number of Al inside the TM icosahedron contribute to the superstructure.


\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Schematic illustration of Al\textsubscript{11}TM\textsubscript{4} phase.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Selected area electron diffraction patterns of (a)Al\textsubscript{72.5}Rh\textsubscript{27.5} and (b)Al\textsubscript{72.5}Ir\textsubscript{27.5}.}
\end{figure}
In this work the estimation of the amount of phason flips in random positions of the Fibonacci chain is done basing on the Average Unit Cell concept [1, 2, 3].

The phenomena called phasons for aperiodic crystals have many different meanings [4]. In this work what we understand as phason is the local rearrangement of structure units known as phason flip. For the purpose of this work we consider \text{LS} \rightarrow \text{SL} swap in the Fibonacci chain sequence. As a consequence of flip occurrence, intensities of the diffraction peaks changes. The change is currently taken into account by introducing Debye-Waller factor with the perpendicular space scattering vector [5]. What we propose is to analyze phasons within the physical space using the statistical approach. Each single tiles rearrangement influence change of the atomic positions distribution, which is characteristic for particular structure. Deviation from the distribution free of the phasons flips can be designated and therefore the amount of flips is quantified.

In order to retrieve the information about the amount of flips we develop power series expansion of the characteristic function of the atomic positions distribution. The characteristic function for quasicrystals is equal to the structure factor. Moments of the distribution are fitted against diffraction data and the value of the second moment gives information about amount of flips in the structure. Higher moments tend to differ from the theoretical calculation (Fig. 1).

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure1}
\caption{Fitted values of the second moment (black square), fourth moment (blue circle) and sixth moment (red triangle) in respect to the flip ratio $\alpha$.}
\end{figure}


We demonstrate atomic-scale chemical mapping using energy-dispersivoscopy (EDS) in scanning transmission electron microscopy (STEM) for the local structural/chemical analysis of ternary Tsai-type approximants which are mostly isostructural to Cd$_6$Yb and Zn$_6$Sc but the detailed structure depends on alloy systems and their compositions [1]. The structural/chemical variation of ternary approximants could affect magnetic and electrical properties [2]. On the basis of STEM-EDS mapping combined with high-angle annular dark-field (HAADF) and annular bright-field (ABF) imaging, the structural/chemical variation of Tsai-type approximants could be successfully visualized at atomic-resolution. The results of the local atomic structures in several Tsai-type approximants are presented.
Development of a single-crystal growth procedure for high quality decagonal quasicrystals is a technical challenge. Both pure and Fe doped (0.1-1.0 at. %) Al-Co-Cu and Al-Co-Ni single crystals with decagonal symmetry up to 5 mm in length and 1.5 mm in diameter have been grown by spontaneous crystallization from a melt (Fig. 1). The initial compositions of the melts correspond to the areas of initial crystallization of the decagonal phases at the pseudo-binary phase diagrams. Phase, structural and chemical analyses revealed high quality of the obtained single crystals. According to the back-Laue analysis the long axis of the crystals coincides with the periodic direction.

The temperature dependence of the resistance both in periodic direction and in the quasiperiodic plane as well as magnetoresistance and magnetization of the obtained samples in external magnetic fields of up to 18 T were studied. Negative magnetoresistance along the periodic direction was observed in the Fe doped samples at low temperature due to Kondo effect (Fig. 2).
ATOMIC STRUCTURE AND DIFFUSE SCATTERING OF TERNARY Yb-Cd-Mg ICOSAHEDRAL QUASICRYSTAL

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A discovery of binary icosahedral (i) quasicrystal (QC) YbCd5.7 achieved a breakthrough and the description of the atomic structure of i-YbCd5.7 is now available [1, 2]. On the other hand, the atomic structure of ternary QCs remains challenging problem because of substitutional disorder cannot be ignored in this case. Recently, it has pointed out the chemical order exits in the ternary i-Yb12Cd36Mg52 as well as periodic 1/1 approximant phases in R-Cd-Mg (R=Pr and Y) [3]. Because it forms in the wide composition range with a constant Yb concentration [4], it is possible to compare the atomic structures contain very different Mg concentrations. This could provide new insights for the stability and formation of the QCs.

The single-grained crystals of i-Yb-Cd-Mg with two different compositions have been prepared. The composition has been analysed by ICP-AES and given by Yb15.2Cd68.4Mg16.1 and Yb15.1Cd38.5Mg46.4. The diffraction experiment has been carried out using in-house X-ray diffraction system (Mo target) and 5166 common unique reflections have been measured. In addition supplemental experiment for diffuse scattering has been carried out on the beamline CRISTAL at the synchrotron SOLEIL. Data reduction including integration and absorption correction has been performed using a computer package CrysAlisPRO and the structure analysis has been performed using QUASI07 [5].

On the diffraction pattern we observed characteristic intensity distributions of diffuse scattering at the positions correspond to F-type superstructure. We also found that Yb15.2Cd68.4Mg16.1 showed sharper diffuse scattering than Yb15.1Cd38.5Mg46.4, which indicates that the F-type s.r.o relates to the concentration and distribution of Mg in the QC structures.

We analysed their average structures (i.e. P-type structure) based on the 6-dimensional (6-D) model of i-YbCd5.7 [2]. In the refined structures we found distinct chemical order for Tsai-type rhombic triacontahedon (RTH) cluster in Yb15.2Cd68.4Mg16.1 rather than in Yb15.1Cd38.5Mg46.4: the icosidodecahedron shell is pure Cd and the threefold edge, fivefold edge and edge canter sites on the RTH shell are pure Cd, Mg and Cd, respectively, for the Yb15.2Cd68.4Mg16.1. On the other hand, we found a substitutional disorder by Cd and Mg on the dodecahedron site, regardless of the Mg concentration in the both samples. The details of resulting structures will be presented and discussed together with the observed diffuse scattering.


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Electron Microscopy Studies of Binary Nanocolloidal Quasicrystals

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Quasicrystalline order has been discovered in many soft matter systems such as self-assembly of dendrimers [1], block copolymers [2], and binary nanocolloidal systems [3]. Most of the systems show dodecagonal quasicrystalline symmetry with the characteristic length of 10 to 100 nm. Binary nanocolloidal crystals made of two different nanoparticles are a promising new class of advanced functional materials with unique synergetic and collective properties. These materials have been shown to exhibit excellent structural diversity and a wide range of different stoichiometries in meso-scale. We have prepared binary nanocolloidal quasicrystals as inorganic bulk materials by simple solvent evaporation of nanocolloidal aqueous solutions. Characterization by electron microscopy and small angle X-ray scattering revealed the detailed structures of the binary nanocolloidal assemblies as well as dodecagonal quasicrystalline symmetry as shown in Fig. 1.


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Figure 1. Electron microscopy image of binary nanocolloidal quasicrystal (a) and its Fourier diffractogram (b).
Crystal structures are commonly described invoking principles of symmetry and close packing. We like to draw attention to another, seemingly less explored idea: the uniform distribution of atoms in space.

Several applications were explored so far: (i) Multiplicative congruential generators devised for the construction of pseudo-random numbers are closely related to crystallographic sublattice structures [1-3], whose uniform distribution properties can be assessed by the so-called spectral test [6]; (ii) Van der Corput’s bit-reversal method used for the construction of quasi-random numbers shows relations to planar quasiperiodic tilings of octa- and decagonal symmetry (Fig. 1, [4]); (iii) A measure for the uniform distribution of point sets, the star discrepancy, is used to discover a variant of the β-Mn structure with local octagonal symmetry upon projection (Fig. 2, [5]); (iv) Another such measure, the diaphony, exhibits relations to the structure factor equation and the Patterson function and thereby connects to the methodology of crystal structure solution from X-ray diffraction experiments [6].

As it seems a rich field of potential interrelations between aspects of uniform distribution theory (e.g. as described in [7]) and (quasi-)crystallography is yet to be uncovered.


Figure 1. Tiling composed of near-miss Penrose and Ammann-Beenker rhombs constructed from the quasi-random van der Corput sequence [4].

Figure 2. Low-discrepancy variant of b-Mn with local octagonal symmetry upon projection [5].
TO BE, OR NOT TO BE, A QUASICRYSTAL: THE STRANGE CASE OF NiZr

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The discovery of quasicrystals by Shechtman et al. about 30 years ago [1] triggered some fierce debate revolving about the existence of this novel and peculiar state of matter, with Linus Pauling as the main opponent willfully explaining away some of the observed electron diffraction features as a phenomenon of multiple twinning. Experimental evidence disproved Pauling’s arguments, while awarding Shechtman the Nobel Prize in Chemistry for the year 2011 seemingly settled the matter. However, the field of complex metallic alloys is always good for a surprise.

Studying the non-equilibrium solidification of the intermetallic glass-former NiZr from a deeply undercooled melt, we reproducibly observed, by means of a high-speed camera, the formation of a decagonal solidification front, traversing atop the surface of a spherical droplet of molten NiZr, processed by electrostatic levitation. A subsequent analysis of the as-solidified microstructure employing electron backscatter diffraction revealed the presence of a multiple twin with a tenfold domain structure, similar to prior observations made by Kuo et al. using high-resolution transmission electron microscopy.[2]

Their model of the tenfold twin is supported by a special axial ratio $a/b \sim 1/3$ found for the CrB-type, orthorhombic crystal structure of NiZr, yielding the expected angle of $\alpha = 2 \tan^{-1}(a/b) \sim 36^\circ$ between neighbouring twin domains, including a proposed relative shift of $(1/4)[100]$. Moreover, Parthé showed that the CrB-type itself can be conceived as resulting from a twinning at the unit-cell level [3], while Andersson et al. popularized the ideas of crystallographic shear and (cyclic) intergrowth structures in order to describe a plethora of complex inorganic crystal structures [4], including a number of derivative structures composed from a basic CrB-type structural motif by locally applying distinct modes of twinning (ibid., p. 236). However, despite this previously known vital ingredients, the recipe is more complex in the case of NiZr.

We propose a distinct model of the tenfold twinning observed in NiZr [5] based on a relative shift of $(\sim 1/6)[100]$, instead, and applied to adjacent twin domains in a circular manner. The model is unique in the sense that it additionally involves a slight idealization of the atomic coordinates, resulting in a very special, deformation-free twin domain boundary locally identical (!) to the bulk structure of NiZr. Moreover, CrB-type NiZr in this special tenfold twinned microstructure gains features of a quasicrystal, especially those of decagonal long-range orientational order including scaling relations based on the golden ratio, blurring the distinction, from a Fourier space point of view, between a multiple twin and a quasicrystal in an intriguing way. Summarizing all the details, we conclude that a quasicrystalline seed nucleates in the undercooled melt of NiZr and proceeds to grow, quite naturally in terms of the proposed structural model, into a highly-coherent tenfold twinned dendritic microstructure on the macroscale.

STRUCTURE OF THE ORTHORHOMBIC $\varepsilon_{16}$ PHASE IN THE Al-Pd-Ru SYSTEM

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The structural information on the crystalline approximants assumes a crucial role for studying atomic structure of quasicrystals. Various orthorhombic $\varepsilon_n$ ($n = 6, 16, 22, 28$) phases, approximants to decagonal quasicrystals, form in several Al based alloys [1]. Among the $\varepsilon_n$ phases, the structure of only $\varepsilon_{6}$ phase was determined by Boudard et al. [2]. Although the structure of $\varepsilon_{16}$ phase was investigated in the Al-Rh system by the strong-reflections approach [3] and in the Al-Pd-Co system by a combination of HREM and single crystal X-ray diffraction [4], no precise structure has been reported so far. In the present work, we solved the structure of $\varepsilon_{16}$ phase in the Al-Pd-Ru system by means of single crystal X-ray diffraction with the specimen extracted from crystals grown by the self-flux method. The $\varepsilon_{16}$ phase belongs to the space group $B2mm$ (No. 38). The refined cell parameters are $a = 23.821(3)$ Å, $b = 16.7183(6)$ Å, $c = 32.71(1)$ Å. The least-squares software of SHELXL was used for the structural analysis [5]. The refinement converged with $R1 = 0.0756$ for the observed 44157 reflections. The projected structure along the $b$ axis can be described with a tiling of banana-shaped nonagon and pentagon (Fig.1), whose edge length is $\sim 7.7$ Å. Pseudo-Mackay icosahedral (PMI) clusters occupy the vertices. A PMI cluster consists of centred Transition-Metal (TM), symmetry-broken inner Al shell, a TM icosahedron and Al icosidodecahedron. Three symmetrically independent PMI clusters doubly-pile up along the $b$ axis in each unit cell. The diameter of the icosahedron is $\sim 8.4$ Å. Adjacent PMI clusters in a plane normal to the $b$ axis are connected via a common two-fold axis ($b$-linkage). Their TM icosahedral shells share edges and the icosidodecahedral shells inter-penetrate each other. Besides, three types of small icosahedral clusters occupy inside each tile.

Figure 1. The structure of Al-Pd-Ru $\varepsilon_{16}$ phase projected along the $b$ axis.


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MELTING PROCESS OF DECAGONAL COLLOIDAL QUASICRYSTALS

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It has been predicted by an extension of the so-called KTHNY theory [1, 2] that melting of two-dimensional quasicrystals occurs in a two step process when increasing the temperature: First, thermally excited dislocation pairs dissociate and as a consequence destroy the quasi-long ranged positional order but not the orientational order. The expected intermediate phase was termed the pentahedral phase [2]. In the second step, the dislocations dissociate into disclinations and the orientational order is destroyed as well.

By using Monte-Carlo and Brownian dynamics simulations, we study the melting process of decagonal colloidal quasicrystals by analysing the positional and bond-orientational correlation functions during the melting process. We observe an intermediate state with quasi-long ranged orientational order but only short ranged positional order. Analysing the ordering of the intermediate state reveals network-like structures of defects spanning through defect-free areas.


CATALYTIC MECHANISM IN QUASICRYSTALS BASED ON LOCALIZED ANHARMONIC VIBRATIONS

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Among many surprising properties of quasicrystals (QCs) is their high catalytic activity [1, 2]. There is no single theory of catalysis, but only a series of principles to interpret the underlying processes. An important parameter of the chemical kinetics is the activation energy, i.e. the energy required to overcome the reaction barrier. The lower is the activation energy, the faster the reaction rate, and so a catalyst may be thought to reduce somehow the activation energy. Recently, it has been shown [3-5] that in a crystalline matrix, the activation energy may be reduced at some sites due to a special class of localized anharmonic vibrations (LAVs) of atoms, known also as discrete breathers [6] or intrinsic localized modes [7]. LAVs can be excited either thermally or by external driving, resulting in a drastic acceleration of the reaction rates in their vicinity. Building upon this recognition, a new paradigm is emerging in the theory of catalysis, whereby LAVs may be viable candidates for catalysts in various systems.

In this context, we present atomistic simulations of LAVs in 1-D QCs and a model of catalysis in QCs that can take place at special sites provided by their inherent topology. A striking site selectiveness of LAV formation in disordered structures like proteins [5] allows one to suggest that their concentration in quasicrystals may be very high as compared to regular crystals where LAVs arise homogeneously, and their activation energy is relatively high. Direct experimental observations [8] have shown that in the decagonal quasicrystal Al\textsubscript{57}Ni\textsubscript{20}Co\textsubscript{23}, mean-square thermal vibration amplitude of the atoms at special sites greatly exceeds the mean value, and the difference increases with temperature. This might be the first experimental observation of LAVs, which have shown that they are arranged in just a few nm from each other. So in this case, one deals with a kind of ‘organized disorder’ that stimulates formation of LAVs, which may explain a strong catalytic activity of some quasicrystals. Verification of this hypothesis can open the new ways towards engineering of catalysts based on computer modeling of LAVs in quasicrystals.

Structural perfection of the Cd-Yb icosahedral quasicrystal phases prepared by different techniques has been studied by single-crystal X-ray diffraction. Two Cd-Yb icosahedral phases have been prepared either by the Bridgeman technique (sample-1) or by slowly cooled from the melt (sample-2), and they were annealed at 673 K for several weeks. High-resolution single crystal X-ray diffraction has been carried out on the JAEA beamline at SPring-8. In addition, supplemental X-ray diffraction data was collected using X-ray Mo source for large reciprocal intensity maps. Diffraction data have been analysed using CrysAlisPRO and all equivalent zero-th reciprocal layers perpendicular to two-, three- and five-fold axes have been reconstructed.

For the sample-1 Bragg peaks were observed at their ideal positions corresponding to the icosahedral symmetry. On the other hand, the sample-2 exhibits Bragg peak shift from their ideal positions, characteristic to a linear phason strain. Figure 1 shows two-fold reciprocal layers are normal to each other for the sample 2. The peak shift is clearly visible on the two-fold layer perpendicular to 0/0 0/0 0/2, which indicates a symmetry breaking for two-fold axes 0/0 0/2 0/0 and 0/-2 0/0 0/0 as well as two mirror planes (0/-2 0/0 0/0) and (0/0 0/2 0/0). Whereas, the peak shift is not clear on the other plane normal to 0/2 0/0 0/0. By checking another reciprocal layers, we found the symmetry of the sample-2 is lower than 2/m.


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