MS63.P14

In situ TEM study of the order-disorder phase transition in Cd_6M approximants at low temperature

Kazue Nishimoto,[a] Takeru Sato,[b] Yasushi Kamimura,[a] Keiichi Edagawa,[a] Ryuji Tamura,[b] *[a]Institute of Industrial Science, the University of Tokyo, Tokyo, (Japan). [b]Department of Materials Science and Technology, Tokyo University of Science, Chiba, (Japan).* E-mail: nishi-mt@iis.u-tokyo.ac.jp

An occurrence of an order-disorder phase transition was first discovered in Cd_6Ca and Cd_6Yb at 100K and 110K, respectively, which has been attributed to orientational ordering of the Cd_4 tetrahedron in the centre of the cluster. A series of Cd_6M (M = Ca, Sr, Rare earth metals) compounds [1,2] are 1/1 cubic approximants to the binary $Cd_{5.7}Yb$ and $Cd_{5.7}Ca$ quasicrystals. Also, Cd_6M possesses a *bcc* lattice made of the Tsai-type icosahedral cluster [3, 4]. The Tsai-type icosahedral cluster is composed of four successive shells, which are, from the centre, a Cd_4 tetrahedron, a Cd_{20} dodecahedron, a M_{12} icosahedron and a Cd_{30} icosidodecahedron. For most Cd_6M (expect for Cd_6Eu and Cd_6Ce), the Cd_4 tetrahedron at the centre is orientationally disordered at room temperature. Among them, Cd_6Ca has been investigated in detail and it has been found that Cd_6Ca transforms into a $\sqrt{2}a \times a \times \sqrt{2}a$ lattice with space group C2/c below 100 K [5]. In the present work, we have investigated superlattice structures and structural relationship between the ordered and disordered phases in a variety of Cd_6M (M = Y, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Tm, Er and Lu) by *in-situ* transmission electron microscopy (TEM) at low temperatures.

In the cases of Cd_6M (M = Y, Pr, Nd, Sm, Gd and Tb), we have observed superlattice reflections at 20 K in the selected area electron diffraction patterns. The superlattice reflections are explained by a $\sqrt{2}a \times a \times \sqrt{2}a$ *C*-centred monoclinic lattice with space group *C2/c* or *Cc* as well as Cd_6Ca. It suggests that the *C*-monoclinic superlattice structures are commonly formed for Cd_6M (M = Ca[5], Y, Pr, Nd, Sm, Gd and Tb). In contrast, for Cd_6Ho, Cd_6Er, Cd_6Tm and Cd_6Lu, which have a smallest atomic radius of M, no superlattice reflection has been observed down to 20 K. The results indicated that no order-disorder phase transition occurs in Cd_6M (M = Ho, Tm, Er and Lu) and the Cd_4 tetrahedron at the centre of the icosahedral cluster remains disordered down to 20 K. The difference in the structure of the low temperature phase is well classified in terms of the atomic radius of M elements, which indicates that the space inside the M_{12} icosahedron plays a dominant role in the ordered phase formation. Results of other TEM observations will be discussed in details.

[1] C.P. Gómez, S. Lidin, Phys. Rev. B **68c**, **2003** 024203. [2] S.Y. Piao, C.P. Gómez, S. Lidin, *Z. Naturforsch* **2006**, *60b,* 644. [2] R. Tamura, Y. Murao, S. Takeuchi, M. Ichihara, M. Isobe, Y. Ueda, *Jpn. J. Appl. Phys.* **2002**, *Part 2 41*, L524. [3] R. Tamura, K. Edagawa, Y. Murao *et al.*, *J. Non-Cryst. Solids* **2004**, 334 & 335 173. [5] R. Tamura, K. Edagawa, K. Shibata *et al.*, Physical Review **2005**, *B 72,* 174211.

Keywords: quasicrystal, transition, TEM

MS63.P15

Decagonal phases in Al-Ni-Rh system

Dmitry Logvinovich, Walter Steurer, *Laboratorium für Kristallographie, ETH Hönggerberg, CH-8093 Zürich.* E-mail: dmitry.logvinovich@mat.ethz.ch

The interest in the Al-Ni-Rh decagonal phase structure is triggered by the fact that it is formed at the Al and Ni concentration where also the extensively studied Al-Ni-Co decagonal phase [1] is stable. Due to the similar number of electrons in Ni (28) and Co (27), X-ray diffraction does not allow distinguishing between these elements and thus solve the latter structure unambiguously. Instead of Co, the new decagonal phase contains Rh (45). The latter also has a larger atomic radius than Co. This will allow studying the important Ni/Rh order in the average structure.

The discovery of decagonal quasicrystals in Al-Ni-Rh system has been recently reported in literature [2]. The structural studies available up to now are limited to high-resolution transmission electron microscopy (HRTEM) and electron diffraction (ED) [2-4]. According to them the reported decagonal phase has a period of 4 Å along the 10-fold axis. No refined structural model of that phase is available up to date.

Recently we have succeeded in growing single crystals of the 4Å-decagonal phase of Al-Ni-Rh system large enough for single crystal diffraction experiments. The crystal structure of that phase has been solved in 5D-space (space group: $P10_5/mmc$) by charge-flipping algorithm. The solution reveals that Rh-atoms preferentially occupy centers of the transition metal atom occupation domains. The diffraction experiments reveal weak diffuse scattering within Bragg layers.

In course of our investigations two other phases were obtained: a new decagonal phase and an approximant with 16Å periodicity along 10- and pseudo-10-fold axes respectively.

[1] A. Cervellino, T. Haibach, W. Steurer, *Acta Crystallogr. Sect. B: Struct. Sci.* **2002**, *58*, 8. [2] K. Tsuda, *Philos. Mag. Lett.* **1996,** *73*, 271. [3] B. Grushko, S. Mi, *Z. Kristallogr.* **2003**, *218*, 389. [4] B. Przepiorzynski, S. Mi, B. Grushko, M. Surowiec, *Intermetallics* **2007**, *15*, 918.

**Keywords: decagonal quasicrystal, approximant, X-ray diffraction**

MS63.P16

Extremely long-period 1d stacking polytypes in $Al_{13}Co_4$

Takehito Seki, Eiji Abe, *Department of Materials Science & Engineering, The University of Tokyo, Tokyo (Japan).* E-mail: seki@stem.t.u-tokyo.ac.jp

Although the Al-Co system has been intensively investigated, there still remains uncertainty regarding the phase formation around the particular composition $Al_{13}Co_4$ [1, 2]. The monoclinic structure m-$Al_{13}Co_4$ and the orthorhombic structure o-$Al_{13}Co_4$ have been well-known as the approximant crystals related to the decagonal quasicrystals. Recently, a new type of orthorhombic structure o'-$Al_{13}Co_4$ was reported by Fleischer et al. [3]. These three types of the $Al_{13}Co_4$ structures can be interpreted according to a different stack of the pentagonal-cluster chains (Fig. 1). In the present paper, we reinvestigated the Al-Co system around $Al_{13}Co_4$ and discovered a new polytype structures with extremely long-period correlation distances.

An ingot of about 10g with the nominal composition of $Al_{76.5}Co_{23.5}$ ($Al_{13}Co_4$) was prepared using arc melting technique under argon atmosphere. Samples were annealed at 950°C, 980°C, 1000°C, 1050°C and 1080°C, respectively. We identified the phases based on electron diffraction patterns (EDPs), finding out that the major phases are o-$Al_{13}Co_4$ at 950°C, o'-$Al_{13}Co_4$ at 1050°C, and m-$Al_{13}Co_4$ at 1080°C. Many unknown EDPs with streaks or superlattice reflections along specific direction are frequently observed for the specimen annealed at 980°C and 1000°C. These EDPs are basically explained as being structural polytypes constructed by a stack of the pentagonal-cluster chain (Fig). The relevant stacking sequence can be determined by direct structural observations using high-angle annular dark-field scanning transmission electron microscopy.

On the basis of careful examinations of diffraction peak appearances, we find a striking feature that the stacking periods are extended into extremely long distances, typically being longer than ~100Å. Furthermore, even though there are many stacking sequences possible for a given periodic length, each of the observed stacking structures can be uniquely determined according to the polytype series generated by a hyperspace crystallography, as combined with an systematic introduction of shear strains for a hyper-cubic crystal. This intriguing fact in turn implies that the occurrence of the present long-period variants is restricted by the hidden order along the hyperspace dimension. For understanding an origin of this restriction in terms of temperature dependence of the length-scale change, we applied axial next-nearest-neighbour ising model to the present polytype structures, by defining the stacking direction parameters with an analogy of up-down spin configurations. According to the Monte Carlo simulations, we are able to reproduce the intense peak shift depending on temperature. This suggests that the second nearest-neighbour interactions play a critical role for realizing the extremely long-period order and perhaps incommensurate aperiodic order.

(a) m-Al$_{13}$Co$_4$ (b) o-Al$_{13}$Co$_4$ (c) o'-Al$_{13}$Co$_4$
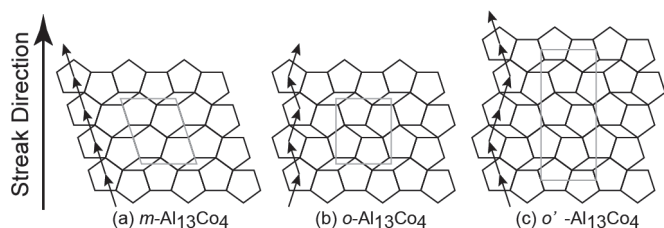
[1] T. Gödecke et al., Z. Metallkde. **1996,** *87,* 854. [2] B. Gruschko et al., *J. Alloys and Comp.* **1996,** *233,* 279. [3] F. Fleischer et al., *J. Alloys and Comp.* **2010,** *500,* 153.

Keywords: quasicrystal, polytype, incommensurate

MS63.P17

Application of average unit cell concept to 3D Amman-kramer tiling

Radosław Strzałka, Bartłomiej Kozakowski, Paweł Kuczera, Janusz Wolny, *Faculty of Physics and Applied Computer Science, AGH University of Science and Technology. Kraków (Poland)* E-mail: radek.strzalka@gmail.com

Amman-Kramer tiling is a 3D generalization of the Penrose tiling. It consists of two kinds of structure units: prolate and oblate rhombohedra with all edge lengths equal. All faces of the structure units are identical rhombuses. The ratio of the face diagonals is equal to τ, and the acute angle amounts to $\arctan(2) = 63.44°$. The volume ratio of the unit tiles as well as the ratio of their frequencies in the tiling also equals τ. Amman-Kramer tiling reveals an icosahedral symmetry, thus it can be used as a quasilattice for building a model of an icosahedral quasicrystal.

One can generate the set of points of the Amman-Kramer tiling by projecting a 6D hypercubic lattice via 3D window – the so called atomic surface. In case of the tiling the atomic surface has the shape of a rhombic triacontahedron (Fig.1).

We present a derivation of the structure factor of the Amman-Kramer tiling on the basis of the average unit cell concept [1], which allows a structure factor calculation in physical space only. This method has been successfully used to perform a structure refinement of the decagonal basic Ni-rich Al-Ni-Co phase [2,3].

Any point of the tiling can be written in the so called reference lattice: $r_i = n_i \cdot \lambda_i + u_i$, $\lambda_i = 2\pi/k_i$, where: $i = x,y,z$, n_i is an integer, λ_i is a reference lattice constant for a given direction and u_i is a position in the reference lattice. The reference lattice constant is related to a scattering vector k_i, which is observed in the diffraction pattern. The position distribution of Amman-Kramer tiling points $P(u_x,u_y,u_z)$ is called an average unit cell (Fig.1). Because of the aperiodicity of the tiling the distribution $P(u_x,u_y,u_z)$ should be related to another one $P(v_x,v_y,v_z)$, whose lattice constants are elongated by τ. A 6D distribution $P(u_x,u_y,u_z,v_x,v_y,v_z)$ is only nonzero along lines: $v_i = -\tau^2 u_i$, This is a characteristic feature of quasicrystalline lattices. One can show that there is a linear relation between the shape of the distribution and the shape of the atomic surface. A structure factor for any scattering vector can be calculated as a Fourier transform of this distribution. It is important to see that because of the characteristic relation between v_i and u_i, the Fourier transform actually reduces to a 3D integral.
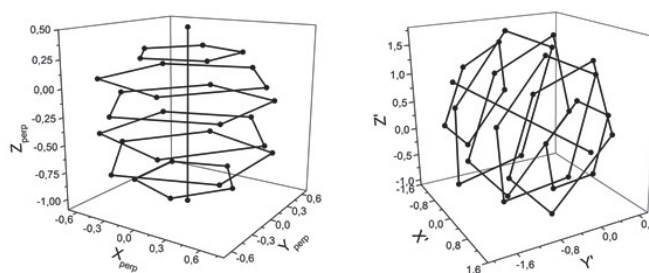

Figure 1. Atomic surface (left) and the average unit cell (right) for Amman-Kramer tiling.

The comparison between structure factors obtained with three methods (numerical calculations, in the perpendicular space and with average unit cell concept) will be presented to show the perfect agreement. The results of first attempts to fit the Cd-Yb [4] experimental data to our model will be discussed.

[1] J. Wolny, *Phil. Mag.* **1998,** 77, 395-412. [2] J. Wolny, B. Kozakowski, P. Kuczera, H. Takakura, *Z. Kristallogr.* **2008**, *223*, 847-850. [3] P. Kuczera, B. Kozakowski, J. Wolny, W. Steurer, *JPCS* **2010**, *226*, 1-7. [4] H. Takakura, C.P. Gomez, A. Yamamoto, M. De Boissieu, A.P. Tsai, *Nature Materials* **2007**, *6*.

Keywords: quasicrystal, structure, modeling.

MS63.P18

Multidimensional paperfolding substitution structures

Dekel Shapira,[a] Shelomo I. Ben-Abraham,[a] Alexander Quandt,[b] [a]*Department of Physics, Ben-Gurion University of the Negev, Beer-Sheba, (Israel).* [a]*School of Physics, University of the Witwatersrand, Wits, (South Africa).* E-mail: nopede@gmail.com

We succeeded to generalize the substitution for the regular one-dimensional paperfolding sequence to two and more dimensions enabling us to construct multidimensional paperfolding structures. We elaborate the algorithm in detail. Here we explicitly present a two-dimensional example of the structure. We display the successive generations using the alphabet {+, ¯} as well as a "realistic" image of a folded paper sheet. We show the calculated Fourier spectrum which is known to have a dense pure point (Bragg) part. We compute the rectangle complexity which is polynomial and hence the entropy vanishes.

Keywords: paper folding structure, substitution