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Acta Cryst. (2011) A67, C627**In situ TEM study of the order-disorder phase transition in Cd₆M approximants at low temperature**

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An occurrence of an order-disorder phase transition was first discovered in Cd₆Ca and Cd₆Yb at 100K and 110K, respectively, which has been attributed to orientational ordering of the Cd₄ tetrahedron in the centre of the cluster. A series of Cd₆M (*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, Cd₆M 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 Cd₄ tetrahedron, a Cd₂₀ dodecahedron, a M₁₂ icosahedron and a Cd₃₀ icosidodecahedron. For most Cd₆M (except for Cd₆Eu and Cd₆Ce), the Cd₄ tetrahedron at the centre is orientationally disordered at room temperature. Among them, Cd₆Ca has been investigated in detail and it has been found that Cd₆Ca 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 Cd₆M (*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 Cd₆M (*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 Cd₆Ca. It suggests that the *C*-monoclinic superlattice structures are commonly formed for Cd₆M (*M* = Ca[5], Y, Pr, Nd, Sm, Gd and Tb). In contrast, for Cd₆Ho, Cd₆Er, Cd₆Tm and Cd₆Lu, 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 Cd₆M (*M* = Ho, Tm, Er and Lu) and the Cd₄ 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 M₁₂ icosahedron plays a dominant role in the ordered phase formation. Results of other TEM observations will be discussed in details.

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Acta Cryst. (2011) A67, C627**Decagonal phases in Al-Ni-Rh system**

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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: *P10₅/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.

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Acta Cryst. (2011) A67, C627-C628**Extremely long-period 1d stacking polytypes in Al₁₃Co₄**

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Although the Al-Co system has been intensively investigated, there still remains uncertainty regarding the phase formation around the particular composition Al₁₃Co₄ [1, 2]. The monoclinic structure *m*-Al₁₃Co₄ and the orthorhombic structure *o*-Al₁₃Co₄ have been well-known as the approximant crystals related to the decagonal quasicrystals. Recently, a new type of orthorhombic structure *o'*-Al₁₃Co₄ was reported by Fleischer *et al.* [3]. These three types of the Al₁₃Co₄ 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 Al₁₃Co₄ 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} (Al₁₃Co₄) 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*-Al₁₃Co₄ at 950°C, *o'*-Al₁₃Co₄ at 1050°C, and *m*-Al₁₃Co₄ 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.