Atomic structures of ternary Yb–Cd–Mg icosahedral quasicrystals and a 1/1 approximant

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Atomic structures of ternary icosahedral (i) Yb–Cd–Mg quasicrystals (QCs) with five different Mg contents up to 46.4 at.% and a corresponding 1/1 approximant (AP), which has a composition of Yb_{13.3}Cd_{70.3}Mg_{16.5}, have been analysed by single-crystal X-ray diffraction. The structures of the iQCs were found to be isostructural to the parent i-YbCd_{5.7}, which consists of a so-called Tsai-type rhombic triacontahedron (RTH) cluster and double Friauf polyhedron, and that of the 1/1 AP was found to be isostructural to YbCd₆, which is described by a body-centred packing of the same type of RTH cluster. In the iQCs, it was found that there are three types of Cd/Mg occupation, namely, Cd preferential site, Mg preferential site and Cd/Mg mixed site, and the occupation probabilities of Mg atoms at the Mg preferential site show a saturation behaviour around the Mg content of 20 at.%. This selective Mg occupation is identified as a cause of the non-linear increase in the icosahedral lattice constant with increasing Mg content. The 1/1 AP has a similar selective Mg occupation to that of the iQCs in terms of the shell structures of the Tsai-type RTH cluster. In both iQCs and the 1/1 AP, the Mg preferential sites have a smaller number of Yb atoms among their coordination numbers. Moreover, short-range order (s.r.o.) diffuse scattering was observed on the diffraction patterns of the iQCs at the positions corresponding to a face-centred-type (*F*-type) icosahedral superlattice. The *F*-type s.r.o. was found to result from the Mg substitution.

1. Introduction

Icosahedral quasicrystals (iQCs) are long-range ordered but lack three-dimensional translational symmetry (Shechtman *et al.*, 1984; Levine & Steinhardt, 1984). ‘Where are the atoms?’ was the first question soon after their discovery (Bak, 1986). The methodology of atomic structure analysis for quasicrystals (QCs) has been establishing step by step in the last few decades (Janssen *et al.*, 2007; de Boissieu, Takakura *et al.*, 2007). However, scientists are still facing a number of hurdles inherent in the QC samples. For example, most QCs with good structural perfection form in ternary alloys such as i-Al–Cu–Fe (Tsai *et al.*, 1987), i-Al–Pd–Mn (Tsai *et al.*, 1990) *etc.*, and thus the structure analysis of QCs has been difficult because a substitutional disorder in atomic occupation must be taken into account in the detailed six-dimensional structure models (Yamamoto *et al.*, 2003; Quiquandon & Gratias, 2006).

In terms of structure analysis, the discovery of stable binary i-YbCd_{5.7} has overcome the problems inherent in the sample in several aspects (Tsai *et al.*, 2000; Guo *et al.*, 2000). First, this phase consists of only two elements, which directly reduces the number of parameters in a refinement of the six-dimensional structure model. Second, there are available 1/1 and 2/1 crystalline approximant (AP) phases located very close to the

iQC phase in the Yb–Cd phase diagram, with the alloy compositions given by YbCd_6 and $\text{YbCd}_{5.8}$, respectively (Pay Gómez & Lidin, 2001, 2003; Takakura, Guo *et al.*, 2001). The atomic structures of these APs consist of the same building units as in the iQC, which provide information crucial for constructing the six-dimensional structure model. Third, according to the atomic structures of these APs, Yb and Cd occupy different atomic sites and these two constituent elements exhibit a good contrast for X-ray scattering, since atomic numbers of the former and the latter are $Z = 70$ and $Z = 48$. Consequently, the only complete structural solution with the six-dimensional structure model has been achieved for $\text{i-YbCd}_{5.7}$ (Takakura *et al.*, 2007). Based on this model, atomic structures of other isostructural binary QCs, such as $\text{i-ScZn}_{7.33}$ and i-RCd ($R = \text{Gd, Tb and Dy}$), have been analysed (Yamada, Takakura, Euchner *et al.*, 2016; Yamada, Takakura, Kong *et al.*, 2016). With the knowledge of the atomic structure of $\text{i-YbCd}_{5.7}$ we can now tackle the structure analysis of ternary iQCs in the same structure type, namely Tsai-type ternary iQCs.

In this study we focus on i-Yb-Cd-Mg for the following three reasons. First, this ternary iQC is thought to be essentially isostructural to $\text{i-YbCd}_{5.7}$ and thus structure refinements can be performed based on the existing $\text{i-YbCd}_{5.7}$ model. Second, the substitution element Mg, whose atomic number is $Z = 12$, exhibits a good X-ray contrast to both Yb ($Z = 70$) and Cd ($Z = 48$). Third, it is known that i-Yb-Cd-Mg has large solid solubility of Mg into Cd up to about 60 at.% (Guo *et al.*, 2002); hence, any correlation between the structural change and the relative occupancies of Cd and Mg can be examined along with Mg content. Such high solubility of the third element into a binary iQC is very rare among known ternary iQCs, which is most likely due to the fact that the atomic radii of Cd (1.57 Å) and Mg (1.60 Å) (Pearson, 1972) are very close. Consequently, the Mg substitution will not lead to much strain in the local atomic structure. In addition, both Cd and Mg are divalent, and the Mg substitution does not change the value of electrons per atom ratio, e/a , which plays a key role in the structure stabilization of iQCs (Tsai, 2004).

To date, no structure refinement has been performed for i-Yb-Cd-Mg . However, it has been shown that the Mg atom replaces specific Cd sites rather than every Cd site randomly. According to the analysis of six-dimensional electron densities for $\text{i-Yb}_{12}\text{Cd}_{36}\text{Mg}_{52}$, the Mg atom substitutes particular Cd sites, *i.e.* the vertices of a rhombic triacontahedron (RTH) shell (Pay Gómez & Tsai, 2013). To determine the detailed atomic occupancies of Cd and Mg and their transitions with Mg contents, full six-dimensional refinements of i-Yb-Cd-Mg structures are necessary.

In this study we performed a systematic structure analysis for the ternary i-Yb-Cd-Mg QCs with various Mg contents, aiming at determining their detailed atomic structures and deriving the preferential occupation sites for Mg upon Cd/Mg substitutions. Refinements of the atomic structures of i-Yb-Cd-Mg based on the $\text{i-YbCd}_{5.7}$ model were performed for the samples with five different Mg contents, ranging from 6.4 to 46.4 at.% of Mg. The refined relative occupancies of Cd and

Mg in terms of the shell structures of Tsai-type RTH clusters have been compared with those of the 1/1 AP which was newly found in this study. In addition, peculiar diffuse scattering intensities, located at the positions corresponding to a face-centred-type (F -type) icosahedral superlattice, have been observed. The origin of the diffuse scattering phenomena is discussed on the basis of chemical short-range order (s.r.o.) between Mg and Cd at the specific preferential sites in the structures.

This article is organized as follows. In §2 we briefly describe the six-dimensional structure model of $\text{i-YbCd}_{5.7}$, since i-Yb-Cd-Mg is essentially isostructural to the former and the structure refinement was performed based on this model. In §3 we describe the experimental details. In §4 we present the results of the sample characterizations. In §5 we present the results of structure analysis of the i-Yb-Cd-Mg QCs and the 1/1 AP, and compare the resulting atomic structures. In §6 we present the results of diffuse scattering measurements and discuss the possible origin of the diffuse scattering phenomena. In the last section, we summarize the important results.

2. Six-dimensional structure model of the $\text{i-YbCd}_{5.7}$ quasicrystal

In the superspace formalism the atomic structure of iQCs is obtained as a result of an irrational cut of the corresponding six-dimensional periodic structure. The six-dimensional structure is described as a six-dimensional lattice decorated with three-dimensional objects, called occupation domains (ODs) or atomic surfaces, lying in the perpendicular (or internal) space, E_{perp} , orthogonal to the parallel (or external or physical) space, E_{par} . In the structure analysis of iQCs, the six-dimensional structure is refined against Bragg reflection intensities [see for instance Yamamoto (1996)].

Fig. 1 shows the six-dimensional structure model of $\text{i-YbCd}_{5.7}$ (Takakura *et al.*, 2007). Fig. 1(a) describes the overall shapes of the ODs, which are projected on E_{perp} , located at the vertex $V:(0,0,0,0,0)$, the centre $C:(1,1,1,1,1)/2$ and the edge-centre $E:(1,0,0,0,0)/2$ of the six-dimensional primitive lattice. The site symmetry of positions V and C is $m\bar{3}5$, and that of position E is $m\bar{5}$. Each OD is obtained from the corresponding asymmetric part shown in Fig. 1(b) by applying the symmetry operations of the site symmetry.

The ODs are defined so as to generate the atomic decoration of the two building blocks of the atomic structure in E_{par} , *i.e.* a Tsai-type RTH cluster and double Friauf polyhedron (DFP) as depicted in Figs. 1(c) and 1(d). Here, the atomic sites and the corresponding ODs are indicated with the same labels, a–m. The atomic site a is at the centre position of the RTH cluster. The cluster consists of five successive atomic shells (from the centre outwards): a Cd_4 tetrahedron, a Cd_{20} dodecahedron, a Yb_{12} icosahedron, a Cd_{32} icosidodecahedron and a decorated Cd_{92} rhombic triacontahedron. The orientation of the central Cd_4 tetrahedron is believed to be disordered at ambient temperature, according to the atomic structures of 1/1 and 2/1 APs (Pay Gómez & Lidin, 2001, 2003; Takakura, Guo

et al., 2001). This shell is thus described in the present model by 20 split-atom positions, which form a small dodecahedron with occupancy equal to 0.20 so that the shell contains four atoms as a whole. The DFP results from the atomic decoration of an acute rhombohedron whose vertex and edge-centre positions are occupied by Cd atoms and the two positions on the longer body diagonal are occupied by Yb atoms. Two Yb atoms (*k* and *l*) can be distinguished, since they are generated from the different parts of the ODs (Fig. 1*b*). The DFPs occupy the interstitial voids of the RTH cluster network. It is important to note that the Cd atoms in a DFP are shared among attached RTHs and/or DFPs.

The RTH cluster network in the i-YbCd_{5.7} model is characterized by two kinds of connections called *b*- and *c*-linkages, along the directions parallel to the twofold and threefold axes, respectively, as depicted in Fig. 1(*e*) (Henley, 1986). The atomic sites denoted by the labels *a*–*l* are distinguished depending on the local environment of the RTH cluster. For the *b*-linkage two neighbouring RTH clusters share a rhombus face. Accordingly, the atomic sites *g* and *i*, which are located at the apexes of the long diagonal and the short diagonal of the shared rhombus, respectively, have different local environments

from the rest of the atomic sites on the RTH shell (Fig. 1*e*). For the *c*-linkage two RTH clusters interpenetrate, by sharing an obtuse rhombohedron (OR), and thus the atomic site *h* is discriminated against other sites on the RTH shell. The atomic site *d* on the vertex of the shorter body diagonal of the shared OR can also be discriminated, since it is associated with both the RTH shell of one cluster and the dodecahedron shell of the adjoining cluster (Fig. 1*e*).

The local configuration of each RTH cluster is expressed by a notation (*N*, *N_b*, *N_c*), where *N* is the coordination number of surrounding RTH clusters, *N_b* and *N_c* are the number of *b*- and *c*-linkages (Henley, 1986). In the i-YbCd_{5.7} model there are 18 local configurations in total, with the two most frequent ones being (12, 7, 5) and (12, 6, 6), representing 24.87% and 24.40%, respectively (Takakura, 2008; Takakura & Strzałka, 2017).

3. Experimental

Yb–Cd–Mg alloys with nominal compositions Yb_{15.5}Cd_{84.5–x}Mg_x (*x* = 5, 10, 20, 30, 40, 50, 60) and Yb₁₃Cd₆₇Mg₂₀ were prepared from the pure elements Yb (99.9 wt%), Cd (99.9999 wt%) and Mg (99.99 wt%). Hereafter, these alloys are denoted as samples 1–8, respectively. The elements weighed with an objective composition were placed inside an alumina crucible and wrapped with a Ta foil. The crucible was then sealed in a silica tube under an Ar atmosphere. The starting elements were heated to 973 K using an electric furnace and the molten state was kept for 12 h; it was then cooled at a rate of -5 K h^{-1} to 673 K and kept for 1080 h inside the furnace for homogenization. The same procedure was applied to all the samples.

The obtained alloys were characterized by powder X-ray diffraction (XRD) at ambient temperature using Cu $K\alpha$ radiation ($\lambda = 1.54084\text{ \AA}$). The microstructure observations were carried out using scanning electron microscopy (SEM) (SU6600, Hitachi). The composition of each sample was determined by inductively coupled plasma atomic emission spectrophotometry (ICP-AES) (ARCOS, SPECTRO). The analysis of composition was also done with energy-dispersive X-ray (EDX) spectroscopy combined with the SEM apparatus. To determine the icosahedral lattice constant, a_{ico} , for each i-Yb–Cd–Mg QC sample, a synchrotron powder XRD experiment at ambient temperature was carried out on a Debye–Scherrer type diffraction system with X-ray wavelengths of $0.6525\text{ \AA}$ for samples 1–4, 6 and 7, and $0.6526\text{ \AA}$ for sample 5 on the BL15XU at SPring-8. Each powdered sample was loaded into a 0.1 mm-diameter Lindemann glass capillary and powder XRD patterns were recorded using an imaging plate. The position resolution of the imaging plate corresponds to the pixel size in scanning. The resolution in reciprocal space is $0.002\text{ \AA}^{-1}$, estimated from the peak profiles of Si powder diffraction. The a_{ico} for each sample was determined by an extrapolation method (Nelson & Riley, 1945).

A single-crystal XRD experiment was performed at ambient temperature on a laboratory single-crystal XRD system equipped with a charge-coupled device (Saturn 724

Figure 1

Six-dimensional model of the i-YbCd_{5.7} QC (Takakura *et al.*, 2007). (*a*) Entire and (*b*) asymmetric parts of occupation domains (ODs) located at the vertex *V*:(0,0,0,0,0,0), the edge-centre *E*:(1,0,0,0,0,0)/2 and the body-centre *C*:(1,1,1,1,1,1)/2 of the six-dimensional lattice. (*c*) Successive shells in the rhombic triacontahedron (RTH) cluster and (*d*) double Friauf polyhedron (DFP). (*e*) *b*- and *c*-linkages of the RTH clusters. Only dodecahedron and RTH shells are shown. The labels *a*–*m* indicate the correspondence relations between the atomic sites and the small ODs.

Table 1

Nominal and analysed compositions of the Yb–Cd–Mg alloys (samples 1–8).

The compositions of samples 1–6 and 8 were determined by ICP-AES, and that of the sample 7 by EDX.

Sample No.	Nominal composition (at.%)			Analysed composition (at.%)		
	Yb	Cd	Mg	Yb	Cd	Mg
1	15.5	79.5	5.0	14.8	83.9	1.3
2	15.5	74.5	10.0	15.2	78.4	6.4
3	15.5	64.5	20.0	15.5	68.4	16.1
4	15.5	54.5	30.0	16.0	58.7	25.3
5	15.5	44.5	40.0	15.8	51.6	32.5
6	15.5	34.5	50.0	15.1	38.5	46.4
7	15.5	24.5	60.0	15.4	26.2	58.4
8	13.0	67.0	20.0	13.3	70.3	16.5

HG, Rigaku) and a partial chi-type goniometer using Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) generated by a rotating-anode-type X-ray generator (FR-X, Rigaku). The single-crystal samples with a size of about 100 µm were picked up from crushed alloys and mounted on thin glass needles. Data collections were performed with sample–camera distances of 55 mm for the iQCs and 45 mm for the 1/1 AP. Indexing of Bragg reflections, integration and absorption corrections for the diffraction intensities were performed utilizing the software *CrysAlis PRO* (Rigaku Oxford Diffraction, 2015). In addition, to explore the intensity distribution in a large volume in reciprocal space, supplemental single-crystal XRD experiments were performed at ambient temperature on the CRISTAL beamline at the synchrotron SOLEIL ($\lambda = 0.51078$ Å) and on the BL22XU beamline at SPring-8 ($\lambda = 0.37380$ Å).

4. Sample characterization

Powder XRD patterns for samples 1–6 could be indexed with a primitive-type (*P*-type) icosahedral lattice, revealing that each sample is a single phase of iQC, which has also been shown by SEM microstructure observations. For sample 7, in addition to the diffraction peaks from a *P*-type iQC, other peaks from a foreign phase were observed. A microstructure observation showed that sample 7 contains a secondary phase which has the composition of approximately $\text{Yb}_{17}\text{Cd}_{33}\text{Mg}_{50}$. On the other hand, the powder XRD pattern for sample 8 agrees well with the calculated pattern of the YbCd_6 1/1 AP (Pay Gómez & Lidin, 2003). The lattice constant was determined to be 15.7531 (1) Å. To the best of our knowledge, this is the first observation of a 1/1 AP phase in the ternary Yb–Cd–Mg system.

Table 1 summarizes the nominal and analysed compositions for the samples. The analysed compositions slightly deviate from the nominal ones, which can be attributed to the evaporation of elements during the melting and annealing process, because of their high vapour pressures.

Fig. 2 shows the evolution of a_{ico} which indicates a systematic increase with increasing Mg content in the i-Yb–Cd–Mg QCs. This behaviour is in good agreement with that

observed in a previous study (Tamura *et al.*, 2003). Since the atomic radius of Mg (1.60 Å) is slightly larger than that of Cd (1.57 Å) (Pearson, 1972), the increase of a_{ico} can be understood by assuming that Mg substitutes Cd sites, provided that the i-YbCd_{5.7} structure is intact. However, the evolution of a_{ico} does not follow a linear relation as expected from Vegard's law. Instead, the curve can be divided into two linear parts, *i.e.* below and above about 20 at.% of the Mg content. This non-linear behaviour in a_{ico} is another indication of the existence of preferential sites for Mg in the i-Yb–Cd–Mg QCs (Tamura *et al.*, 2003).

As in periodic crystals, uniform strain in an iQC results in peak broadening of Bragg reflections, and each peak width is scaled with the parallel component of the six-dimensional scattering vector, Q_{par} , which corresponds to a scattering vector in conventional three-dimensional crystals. In addition, the following two factors related to phasons, intrinsic to QCs, lead to significant changes in the Bragg reflections (Lubensky *et al.*, 1986; Horn *et al.*, 1986; Socolar & Wright, 1987; Lubensky, 1988; de Boissieu, Currat *et al.*, 2007). The first one is 'uniform phason strain' which gives rise to peak shifts from their ideal positions, *i.e.* it brings about a symmetry lowering from icosahedral symmetry, and each of the displacements is proportional to the perpendicular component of the six-dimensional scattering vector, Q_{perp} . The second one is 'phason strain distribution', which also brings about a peak broadening and the width is scaled with Q_{perp} . In the synchrotron powder XRD patterns, there were no observations of peak shifts within the experimental accuracy and no signature of peak broadening depending on Q_{perp} for the observed reflections having Q_{perp} up to 2 r.l.u. (reciprocal-lattice unit). Here, the r.l.u. is used as the length scale in reciprocal space. The value in units of Å^{−1} is obtained by multiplying the value in r.l.u. by $2\pi/a_{6D}$, where $a_{6D} = a_{\text{ico}}2^{1/2}$ is a six-dimensional lattice constant. The synchrotron powder XRD demonstrates that the present iQC samples have good

Figure 2
Icosahedral lattice constant (a_{ico}) as a function of Mg concentration for the i-Yb–Cd–Mg QCs. Two linear relations are indicated by dashed lines. Mg concentrations determined by ICP-AES are plotted as filled circles and those determined by EDX as open circles.

crystal perfection in terms of ‘uniform phason strain’ and ‘phason strain distribution’, and have ideal icosahedral symmetry.

Moreover, it is of interest to note that there is a relation between the six-dimensional lattice constant of iQCs and the lattice constant of the cubic APs in the superspace formalism, $a_{p/q} = [2/(2 + \tau)]^{1/2}(q + p\tau)a_{6D}$, where $a_{p/q}$ is the lattice constant for cubic p/q AP (Elser & Henley, 1985). The value of a_{6D} is estimated to be 8.092 Å from the cubic lattice constant of the 1/1 AP (sample 8) and this a_{6D} is close to the experimental a_{6D} of the iQC (sample 3) whose composition is close to that of the 1/1 AP.

5. Structure analysis

5.1. Single-crystal X-ray diffraction

Fig. 3 shows the reciprocal-space sections perpendicular to twofold, threefold and fivefold axes for i-Yb_{15.5}Cd_{68.4}Mg_{16.1} (sample 3) as an example, and the corresponding twofold, threefold and pseudo-fivefold sections for the Yb_{13.3}Cd_{70.3}Mg_{16.5} 1/1 AP (sample 8), which were obtained by reconstructions from laboratory single-crystal XRD data. There are two major indexing schemes for the diffraction patterns in iQCs; these were proposed by Elser (1985) and Cahn *et al.* (1986). The former is used in this paper because we used the computer package *QUASI07_08* (Yamamoto, 2008) which uses this setting.

For the i-Yb–Cd–Mg QCs (samples 2–6), more than 300 000 Bragg reflections in total were observed for each sample with the resolution limit equal to approximately 0.5 Å, and all the peaks could be indexed with a P -type icosahedral lattice. The data reduction was performed assuming the space group $Pm\bar{3}5$ and the same number of 3083 unique reflections for each sample was obtained. The maximum Q_{perp} for the observed reflections was approximately 2 r.l.u. The resulting internal reliability factors (R_{int}) ranged from 0.037 to 0.044. In addition to the Bragg reflections, characteristic arc diffuse scatterings are noticed on the twofold section (Fig. 3a). These diffuse scatterings are indicated by the labels D and E lying on the threefold and fivefold axes, respectively, on the figure. The centres of the arc diffuse scatterings cannot be indexed with the P -type icosahedral lattice, and the intensity distribution of the arc diffuse scatterings was found to be dependent on the Mg content. The details of the diffuse scattering phenomena and their analyses will be given in §6. In the following section, we take only Bragg reflections into account for the structure analyses of i-Yb–Cd–Mg QCs.

For the Yb_{13.3}Cd_{70.3}Mg_{16.5} 1/1 AP (sample 8), 46 476 Bragg reflections in total were observed with the resolution limit equal to approximately 0.5 Å and could be indexed with a body-centred cubic lattice. The data reduction was performed assuming the space group $Im\bar{3}$ and resulted in 3097 unique reflections with $R_{\text{int}} = 0.0604$.

Figure 3

Reciprocal-space sections perpendicular to (a) a twofold, (b) a threefold and (c) a fivefold direction for the i-Yb_{15.5}Cd_{68.4}Mg_{16.1} QC (sample 3), and those perpendicular to (d) a twofold, (e) a threefold and (f) a pseudo-fivefold [8 13 0] direction for the Yb_{13.3}Cd_{70.3}Mg_{16.5} 1/1 AP (sample 8), reconstructed from laboratory single-crystal X-ray diffraction data. The strong reflections labelled by A, B and C, respectively, in (a) are indexed as 20 $\bar{1}$ 012, 21 $\bar{1}$ 11 $\bar{1}$ and 201001 after the index scheme by Elser (1985). The labels D and E indicate the arc diffuse scatterings.

5.2. Structure analysis of the quasicrystals

Using the same number of 3083 unique reflections common to i-Yb–Cd–Mg (samples 2–6), *ab initio* phasing of the

diffraction data for each iQC was carried out using the low-density elimination method, utilizing the program *lodemac* (Takakura, Shiono *et al.*, 2001). Six-dimensional electron densities were then obtained by Fourier syntheses using the retrieved phases and structure-factor amplitudes, utilizing the program *qcmem* in the *QUASI07_08* package (Yamamoto, 2008).

Fig. 4 juxtaposes electron-density distributions on the two-dimensional plane sections of the resulting normalized six-dimensional electron densities, obtained by a cut through the planes defined by fivefold, threefold and twofold axes both in E_{par} and E_{perp} , respectively, for i-YbCd_{5.7} (Takakura *et al.*, 2004, 2007), i-Yb_{15.5}Cd_{68.4}Mg_{16.1} (sample 3) and i-Yb_{15.1}Cd_{38.5}Mg_{46.4} (sample 6). The overall distribution of the electron densities is similar to that obtained for i-YbCd_{5.7}, which verifies that the i-Yb–Cd–Mg QCs are essentially isostructural to the i-YbCd_{5.7} QC. However, systematic decreases in the electron densities as the Mg content increases have been observed at particular positions on the two-dimensional plane sections. These decreases in electron

densities are due to the Mg substitutions, since the atomic number of Mg is 4 and 5.8 times smaller than that of Cd and Yb, respectively.

The electron-density distribution centred at V:(0,0,0,0,0,0) and elongated along E_{perp} , enclosed within the ellipses outlined by a red dotted line in Figs. 4(a) and 4(d), respectively, corresponds to the large OD V in Fig. 1. The decrease in the electron densities on the OD V implies that Mg occupancies increase on the dodecahedron shell and on the fivefold and threefold vertices on the RTH shell. The electron-density distribution centred at C:(1,1,1,1,1,1)/2 and elongated along E_{perp} corresponds to the large OD C in Fig. 1. The decrease in the electron densities at the outer region on the OD C on the twofold section, enclosed within the ellipse outlined by the yellow dotted line in Fig. 4(g), implies that Mg occupancy increases on the Cd₃₂ icosidodecahedron shell. In contrast, the electron-density distribution centred at E:(1,0,0,0,0,0)/2, which corresponds to the large OD E in Fig. 1, remains unchanged. This indicates that Cd atoms on the edge-centres on the RTH shell do not get replaced by Mg atoms. These observations are

Figure 4

Sections of the six-dimensional electron-density distribution cut along planes containing fivefold (top), threefold (middle) or twofold (bottom) axes both in parallel space, E_{par} , and perpendicular space, E_{perp} : (a), (d), (g) for i-YbCd_{5.7} (Takakura *et al.*, 2004, 2007); (b), (e), (h) for i-Yb_{15.5}Cd_{68.4}Mg_{16.1} (sample 3); and (c), (f), (i) for i-Yb_{15.1}Cd_{38.5}Mg_{46.4} (sample 6).

consistent with a previous report on i-Yb₁₂Cd₃₆Mg₅₂ (Pay Gómez & Tsai, 2013).

In addition, by a close inspection of the six-dimensional electron densities, we found splits of the electron densities in the Yb–Cd–Mg QCs, which correspond to particular ODs, as follows. (i) The electron densities, indicated by the white arrowheads in Fig. 4(e), split into two parts and shift along the threefold axis in E_{par} on this section. This means that split-atom sites exist on the dodecahedron shell and the shell is deformed along the threefold directions. (ii) The electron densities, indicated by the open white arrowhead in Fig. 4(h), split into two parts along the twofold axis in E_{par} , which is the perpendicular direction to the section. These split electron densities correspond to the split-atom sites on the icosidodecahedron shell, and suggest that each split occurs perpendicular to a radial direction. The apparent decrease in the electron densities in Fig. 4(h) can thus be understood not only by the Mg occupation of the corresponding OD, but also by the fact that the split densities are located outside of the present twofold section. These results indicate that the positional disorder has to be taken into account in addition to the occupational disorder in the structure analysis of i-Yb–Cd–Mg QCs.

Structure refinements based on the six-dimensional model of i-YbCd_{5.7} (Takakura *et al.*, 2007) have been carried out by the method of least squares against 3083 unique reflections, which are a common number of reflections to samples 2–6 with different Mg contents, utilizing *qcdiff* in the *QUASI07_08* package (Yamamoto, 2008). The model is described by the three large ODs which are generated from their asymmetric parts by symmetry operations as shown in Fig. 1. For a quasicrystal structure refinement, the asymmetric part of a large OD, such as V in Fig. 1(b), is divided into several smaller parts. The partitioning is somewhat arbitrary and the number of parameters for the model depends on the total number of such small ODs. In the present study, the partitioning has been performed so as to discriminate atoms with different local environments, considering up to the nearest-neighbour RTH cluster connections, namely *b*- and *c*-linkages.

Each small OD has the following structural parameters which are refinable in the course of structure refinement: shifts u_1 , u_2 and u_3 of the OD from its initial position along three directions in E_{par} not parallel to each other; *B* factor (or temperature factor in the usual sense) in E_{par} ; perpendicular *B* factor (or phason temperature factor) which takes into account the effect of long-wavelength phason fluctuations on the large ODs along E_{perp} (Kalugin *et al.*, 1985; Levine *et al.*, 1985); occupancies p , s_1 and s_2 , where p describes an occupation probability in the usual sense, and s_1 and s_2 describe partial occupation probabilities for the second and third elements, respectively. The occupancy of each element on a small OD is obtained by combining the total occupancy and the partial occupation probabilities p , s_1 and s_2 as follows: the first element by $p(1 - s_1 - s_2)$, the second element by ps_1 and the third element by ps_2 . Besides the above structural parameters, scale and two extinction parameters are included in the refinement.

The effect of phason fluctuations on structure-factor calculations appears as a multiplication factor, $\exp(-Q_{\text{perp}}^2 B_{\text{perp}}/4)$, where $B_{\text{perp}} = 8\pi^2 \langle R_{\text{perp}}^2 \rangle$ and $\langle R_{\text{perp}}^2 \rangle$ is a mean-square displacement of OD in E_{perp} , similar to the *B* factor in E_{par} (Kalugin *et al.*, 1985; Levine *et al.*, 1985).

In this series of refinements, we made an assumption that the Yb atoms on the icosahedron shell and two Yb atoms inside the DFP persist unchanged upon the Mg substitution, since the electron densities at the corresponding positions, which are around the centre of the six-dimensional lattice on the fivefold and threefold sections, remain unchanged. There is however a report that the solubility limit for Yb in i-Yb–Cd–Mg is about 20 at.%, which exceeds 15 at.% in i-YbCd_{5.7} (Guo *et al.*, 2002). This suggests that Yb atoms can occupy other sites besides the original Yb sites mentioned above. Indeed, the results of ICP analysis of the present i-Yb–Cd–Mg samples indicated that the Yb concentration ranges from 14.8 to 16.0 at.%. To explain the extra Yb concentration of ~ 1 at.% compared with the Yb content in the original i-YbCd_{5.7} model, cluster centre position was included as another possible Yb site, since some 1/1 APs, such as YbZn₆ (Fornasini *et al.*, 2008) and Yb_{16.0}Au_{63.5}Ge_{20.5} (Deguchi *et al.*, 2015), show partial Yb occupation at this position. Therefore, the occupancy of the Yb atom at the cluster centre position, which is generated by the OD labelled a in Fig. 1(b), was taken into account in the refinements.

In addition, unit weights were used in the refinements. In the case of iQCs, the accurate estimation of σ for each unique reflection is difficult because of the multiple diffraction effect. This effect is serious for weak reflections which account for most of the observed reflections. Therefore, using $1/\sigma^2$ weights with incorrect σ 's may result in unnecessary bias against the refined structure.

The resulting reliability (*R*) factors are 0.1167, 0.1423, 0.1494, 0.1456 and 0.1365 for samples 2–6, respectively. The refined alloy compositions are, respectively, Yb_{15.80}Cd_{77.86}Mg_{6.34}, Yb_{15.91}Cd_{67.96}Mg_{16.13}, Yb_{16.12}Cd_{58.46}Mg_{25.43}, Yb_{16.02}Cd_{51.33}Mg_{32.65} and Yb_{15.75}Cd_{38.15}Mg_{46.10}, which are in good agreement with the ones determined by the ICP analysis listed in Table 1. The crystallographic information and parameters for data collection and structure refinement are given in Table 2. Plots of observed and calculated structure factors, the atomic coordinates of refined atomic structures and structure factors for i-Yb–Cd–Mg are provided in the supporting information.

Fig. 5 shows relations between Mg content and the relative occupancies for Yb, Cd and Mg on each OD. From the relations three different types of atomic occupation are found on the ODs: (type I) Mg atom preferentially occupies the ODs b, g, h and i in Fig. 1(b), since the relative Mg occupancy rapidly increases at Mg contents below 20 at.%; (type II) a mix of Cd/Mg occupies the ODs c, d and f, since the relative Mg occupancy gradually increases with increasing Mg content; (type III) Cd atom preferentially occupies the ODs j, since this OD is occupied by pure Cd. When compared with the evolution of the lattice constant a_{ico} with the Mg content shown in Fig. 2, the linear increase in a_{ico} up to Mg contents of

Table 2

Crystallographic information and parameters for data collection and structure refinement for the i-Yb–Cd–Mg QCs (samples 2–6).

For all samples: $T = 293$ K; space group $Pm\bar{3}5$; irregular crystal form, crystal size of $100 \times 100 \times 100$ μm ; Rigaku Saturn 724 HG CCD area-detector diffractometer with Mo $K\alpha$ radiation; data collected with ω scans; empirical absorption correction; unit weight for weighting scheme.

	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
Crystal data					
a_{ico} ($\text{\AA}$)	5.6916 (2)	5.6992 (1)	5.7136 (2)	5.7331 (1)	5.7589 (1)
$F(000)$	3133	2899	2680	2521	2230
Data collection					
Range of θ ($^\circ$)	2.6–43.8	2.6–43.8	2.6–43.9	2.0–43.8	2.5–43.7
Independent reflections	3093	3086	3133	3161	3167
$T_{\text{min}}, T_{\text{max}}$	0.5612, 1	0.6176, 1	0.5213, 1	0.3967, 1	0.4669, 1
R_{int}	0.044	0.040	0.038	0.037	0.040
Refinement					
Refined composition	$\text{Yb}_{15.80}\text{Cd}_{77.86}\text{Mg}_{6.34}$	$\text{Yb}_{15.91}\text{Cd}_{67.96}\text{Mg}_{16.13}$	$\text{Yb}_{16.12}\text{Cd}_{58.46}\text{Mg}_{25.43}$	$\text{Yb}_{16.02}\text{Cd}_{51.33}\text{Mg}_{32.65}$	$\text{Yb}_{15.75}\text{Cd}_{38.15}\text{Mg}_{46.10}$
Point density ($\text{\AA}^{-3}$)	0.044003	0.043631	0.043261	0.042760	0.042490
No. of parameters	130	132	113	108	128
$R(F)$, $F \geq 3\sigma(F)$	0.1167	0.1423	0.1494	0.1456	0.1365
$wR(F)$, $F \geq 3\sigma(F)$	0.0657	0.0782	0.0878	0.0831	0.0648
Residual electron density	$ \Delta\rho < 0.018\rho_{\text{max}}$	$ \Delta\rho < 0.036\rho_{\text{max}}$	$ \Delta\rho < 0.028\rho_{\text{max}}$	$ \Delta\rho < 0.019\rho_{\text{max}}$	$ \Delta\rho < 0.038\rho_{\text{max}}$

20 at.% can be attributed to the ‘type-I occupation’, whereas further increase in a_{ico} with a larger gradient over the Mg contents of 20% can be understood by an increase in the ‘type-II occupation’.

The atomic occupations on the ODs in the refined six-dimensional structure models described above result in the following shell structures of the Tsai-type RTH cluster: (i) the central tetrahedron shell, labelled by b in Fig. 1(c), is preferentially occupied by Mg, when the Mg concentration in the sample becomes larger than 16 at.%; (ii) the dodecahedron shell, labelled by c and d, and the icosidodecahedron shell, labelled by f, are occupied by a mix of Cd/Mg, and the relative Mg occupancies increase as the amount of Mg substitution increases; (iii) the edge-centres of the RTH shell, labelled by j, are occupied by pure Cd regardless of the Mg concentration; (iv) the vertices on the RTH shell, labelled by g, h and i, are found to be Mg preferential sites. In addition, an extra atomic position was found at the cluster centre position, labelled by a, which is occupied by Yb, and the maximum occupancy of this site is equal to 0.23 (1) (Fig. 5a). Another extra atomic position, which is located on the middle of the c-linkage and not included in the original i-YbCd_{5.7} model, was also considered in the refinements, since atomic occupation at this position is observed in the PrCd₆ 1/1 AP (Pay Gómez & Lidin, 2003). The refinements gave the result that Cd occupies this position with a relative occupancy of 0.41 (1) at a maximum provided that it is occupied by pure Cd (lower-right corner in Fig. 5). Details of the resulting atomic structures of the i-Yb–Cd–Mg QCs are described later and they are compared with that of the Yb–Cd–Mg 1/1 AP.

Fig. 6 shows the relation between the refined B_{perp} and the Mg content in the i-Yb–Cd–Mg QCs. The B_{perp} decreases from 1.53 (7) to 1.2 (1) as the Mg content increases from 6.40 at.% (sample 2) to 25.26 at.% (sample 4), and then the B_{perp} increases to 1.92 (9) with further increase in the Mg content up to 46.4 at.% (sample 6). The corresponding values of

$(\langle R_{\text{perp}}^2 \rangle)^{1/2}$ for samples 4 and 6 are 0.12 (1) and 0.156 (4), which are evaluated as approximately 7.6 and 9.6% fluctuations of the triacontahedral OD for the present three-dimensional icosahedral lattice, respectively. This result indicates that the phason fluctuation is dependent on the Mg substitution, and the fluctuation takes the minimum value around 20 at.% of Mg substitution.

We see the following microscopic origin to explain the phason fluctuation which is sensitive to the Mg substitution. As we have found in the refinements, there are two types of atomic occupation along the threefold axis of the large OD V in Fig. 1: one is a part of the preferential OD, labelled by h and i, for Mg (type-I occupation) and the other is a part of the OD, labelled by c and d, for a mix of Cd/Mg (type-II occupation). There will be an exchange between Cd and Mg atoms, when the cut by the parallel space, E_{par} , moves along the threefold direction in E_{perp} ; the replacement of Cd atoms by Mg atoms is coupled with the phason fluctuation. Since the fluctuation is occurring along threefold axes, it may contribute to the phason diffuse scattering elongated along the directions parallel to the threefold axes, which will be shown in §6.

5.3. Structure analysis of the 1/1 approximant

The initial structure model for the Yb_{13.3}Cd_{70.3}Mg_{16.5} 1/1 AP (sample 8) was constructed from the electron densities obtained after *ab initio* phasing of the diffraction data by using the charge-flipping method (Oszlányi & Sütö, 2004, 2005), utilizing the program *SUPERFLIP* (Palatinus & Chapuis, 2007). The structure, which consists of seven inequivalent sites, M1–6 and Yb1, was found to be isostructural to the Ru₃Be₁₇ 1/1 AP (Sands *et al.*, 1962). The structure can also be described as a body-centred packing of Tsai-type RTH clusters which consist of the following four successive shells (from the centre outwards): an M_{20} dodecahedron shell that consists of $M2(24g)$ and $M4(16f)$; a Yb₁₂ icosahedron shell of Yb1(24g);

an M_{32} icosidodecahedron shell of $M3(48h)$ and $M5(12d)$; an M_{92} RTH shell of $M1(24g)$, $M6(12e)$, and some sites on the dodecahedron and the icosidodecahedron shells, $M3$ and $M4$.

Figure 5
Relations between the Mg concentration and the refined relative occupancy of Yb or Mg and/or Cd atoms on each small OD for the i-Yb-Cd-Mg QCs. The labels from a to d and from f to j are the same as those in Fig. 1. The plot with no label (lower-right corner) indicates the occupancy of the Cd atom on the mid-edge site of c -linkages.

The $M5$ and $M6$ were assigned to Mg sites, and $M1$ – 4 to Cd sites in the initial model.

The refinement of the atomic structure parameters and secondary extinction parameter was carried out using *JANA2006* (Petříček *et al.*, 2014), against 2769 unique reflections larger than $3\sigma(F_o^2)$. After iterations of the refinement, difference Fourier syntheses yielded residual peaks at 0.086, 0.05, 0.05 (48h) and 0.24, 0.24, 0.24 (16f). From now on, we call these sites $M7$ and $M8$, respectively. $M7$ corresponds to the atomic positions of the first shell in the YbCd_6 1/1 AP, and $M8$ corresponds to the fractional sites located on the middle of the line which connects the origin and body-centre positions in the PrCd_6 1/1 AP (Pay Gómez & Lidin, 2003).

In a modified model, we included the $M7$ and $M8$ sites with the following two assumptions: (i) a mixture of Cd and Mg occupies $M7$ and the occupation probability is fixed to 1/6, so that four atoms in total exist at the cluster centre, following the YbCd_6 1/1 AP (Pay Gómez & Lidin, 2003); (ii) a fractional Cd occupies $M8$. Assumption (ii) is reasonable because the estimation of partial occupancy of a light atom (Mg) is strongly affected by the presence of a vacancy when the light atom shares the site with a heavy atom (Cd). After iterations of the refinement, $M1$ and $M2$ were found to be occupied by pure Cd, and $M3$ and $M4$ were found to be occupied mostly by Cd, whereas $M5$ – 7 were found to be preferential sites for Mg. Here, the relative occupancy of Cd/Mg at $M7$ and fractional occupancy of Cd at $M8$ were refined and anisotropic atomic displacement parameters (ADPs) were used for all sites except for $M7$ for which an isotropic ADP was used. The refinement was finalized using *SHELXL* (Sheldrick, 2015) against 2904 unique reflections larger than $2\sigma(F_o^2)$, and converged with reliability (R) factors $R1 = 0.0685$, $wR2 = 0.1721$ and $S = 1.073$ (refinement 1). Here, the weight w was estimated by the following equation:

$$w = 1/[\sigma(F_o^2)^2 + (aP)^2 + bP], \quad (1)$$

where $a = 0.0694$, $b = 335.46$ and $P = (F_o^2 + 2F_c^2)/3$. The refined composition is $\text{Yb}_{14.19}\text{Cd}_{67.22}\text{Mg}_{18.59}$ which agrees well with the result from the ICP analysis. The structure, however, exhibits high residual peaks in the difference Fourier map at

Figure 6
Refined perpendicular B factor (B_{perp}) as a function of Mg concentration in the i-Yb-Cd-Mg QCs. The dotted line is a guide to the eye.

Table 3

Crystallographic information and parameters for data collection and structure refinement (refinement 2) for the $\text{Yb}_{13.3}\text{Cd}_{70.3}\text{Mg}_{16.5}$ 1/1 AP (sample 8).

Crystal data	
Formula	$\text{Yb}_{24}\text{Cd}_{113.75}\text{Mg}_{31.37}$
Molar mass (g mol^{-1})	17704.09
Temperature of measurement (K)	293
Space group	$Im\bar{3}$ (No. 204)
a (Å)	15.7531 (1)
Cell volume (Å ³)	3909.29 (3)
Crystal form	Irregular
Crystal size (µm)	100 × 100 × 100
Z	1
$F(000)$	7517.2
Calculated density (g cm^{-3})	7.520
Data collection	
Radiation type	Mo $K\alpha$
Detector	CCD, Saturn 724 HG, Rigaku
Data collection method	ω scans
Range of θ (°)	1.8–46.4
Independent reflections	3097
Observed reflections, $F^2 \geq 2\sigma(F^2)$	2904
Absorption correction	Empirical
$T_{\min}$, $T_{\max}$	0.374, 1
Refinement	
Refined composition	$\text{Yb}_{14.20}\text{Cd}_{67.24}\text{Mg}_{18.57}$
R_{int}	0.0604
No. of parameters	80
R , $F^2 \geq 2\sigma(F^2)$	0.0295
$wR2$, all data	0.0698
S	1.174
$\rho_{\max}$, $\rho_{\min}$ (e Å^{-3})	2.516, −2.489

the positions near the atomic sites which form the dodecahedron and the icosidodecahedron shells: a peak with 6.6 e Å^{-3} 0.53 Å from $M2$, a peak with 10.5 e Å^{-3} 0.58 Å from $M3$ and a peak with 12.5 e Å^{-3} 1.1 Å from $M4$. This result implied the existence of positional disorder on these sites. In addition, this structure also exhibits a residual electron peak with 5.30 e Å^{-3} at the cluster centre, which can be attributed to the partial Yb occupation at this position.

In a further modified model, we split $M2$ into $M2a$ and $M2b$, $M3$ into $M3a$ and $M3b$, and $M4$ into $M4a$, $M4b$ and $M4c$, and set the sums of the occupation probabilities for these sites equal to unity. In addition, mixtures of Cd and Mg were assigned to $M2$ – 4 with the same ratios as those obtained in refinement 1, i.e. $\text{Cd/Mg} = 1/0$ (for $M2a$, $M2b$), $0.92/0.08$ (for $M3a$, $M3b$), $0.88/0.12$ (for $M4a$, $M4b$, $M4c$), respectively, and they were fixed throughout the refinement. The occupancies for the split sites for $M2$ – 4 were refined together with anisotropic ADPs, and the initial values for the other parameters were inherited from refinement 1. Moreover, the occupation probability for the central Yb atom was also refined. The refinement converged with $R1 = 0.0295$, $wR2 = 0.0698$ and $S = 1.174$ (refinement 2). Here, the weight w was estimated by equation (1) with $a = 0.0229$ and $b = 33.8795$. The refined composition is $\text{Yb}_{14.20}\text{Cd}_{67.26}\text{Mg}_{18.55}$ which agrees well with the result from the ICP analysis. The introduction of the split sites for $M2$ – 4 resulted in lower R factors than those in refinement 1. Thus, it can be concluded that the positional disorder is

essential to describe the average atomic structure. The crystallographic information and parameters for data collection and structure refinement are given in Table 3. The atomic coordinates, site occupation factors (s.o.f.s) and the equivalent isotropic ADPs are given in Table 4, and the anisotropic displacement parameters are given in Table 5. The crystallographic information for the refined atomic structure and structure factors for the $\text{Yb}_{13.3}\text{Cd}_{70.3}\text{Mg}_{16.5}$ 1/1 AP (sample 8) are given in the supporting information. We note here that the refined occupation probability of the central Yb atom is very low, 0.005 (4); however, a refinement without the central Yb atom resulted in a residual peak with 4.01 e Å^{-3} , which prompted alert level A in *checkCIF*.

Fig. 7(a) shows the shell structures of the Tsai-type RTH cluster in the resulting atomic structure obtained from refinement 2, and Figs. 7(b)–7(d) show electron-density isosurfaces in parts of the structure obtained by a maximum entropy method, utilizing the software *Dynomia* (Momma *et al.*, 2013), with R factors $R = 0.019378$ and $wR = 0.019978$. The features of occupational and positional disorder in terms of respective atomic shells are as follows. The first shell is described in the model structure by 24 equivalent split positions ($M7$) and a central position. Since the occupation probability of the Yb at the centre is very low, we assume here that the cluster centre is occupied by a total of four atoms, namely, three Mg atoms and one Cd atom. The four atoms would form a trigonal pyramid with a Cd atom at the top and three Mg atoms at the base. The electron densities around $M7$ (Fig. 7b) concentrate at the vertices of a cube with an edge length of 2.1 Å . Because the length is too short for a realistic interatomic distance, the neighbouring positions on the cube cannot be occupied by any atoms at the same time. The electron densities of the first shell are thus interpreted as an average of eight trigonal pyramids oriented along $\langle 111 \rangle$ directions as depicted in Fig. 7(e). This site is considered as a preferential site for Mg. The second dodecahedron shell consists of two inequivalent sites $M2$ and $M4$, which are both Cd preferential sites. The former is composed of two split positions which have a distance of 0.3 Å , and the corresponding electron-density isosurface is shown Fig. 7(c). The latter is composed of three split positions which have a whole split distance of 1.1 Å , and the the corresponding electron-density isosurface (Fig. 7d) shows a large elongation along one of the $\langle 111 \rangle$ directions. This peculiar electron-density distribution is interpreted reasonably as a result of orientational disorder of the central trigonal pyramid. The third shell ($\text{Yb}1$) consists of 12 Yb atoms, which form an icosahedron with an average edge length of $5.8497 (5) \text{ Å}$. The deviation from an ideal icosahedron is much smaller than that observed for the other shells in the RTH cluster. The fourth icosidodecahedron shell consists of two inequivalent sites $M3$ and $M5$, where $M3$ is preferentially occupied by Cd, whereas $M5$ is preferentially occupied by Mg. The site $M3$ is composed of two split positions which have a distance of $0.292 (9) \text{ Å}$, and its corresponding electron-density isosurface can be seen in Fig. 7(d). The outermost RTH shell consists of two inequivalent sites $M1$ and $M6$, where $M1$ is occupied by pure Cd, whereas $M6$ is

Table 4

Atomic coordinates, site occupation factor (s.o.f.) and equivalent isotropic displacement parameters ($\text{\AA}^2$) for the $\text{Yb}_{13.3}\text{Cd}_{70.3}\text{Mg}_{16.5}$ 1/1 AP (sample 8) from refinement 2.

Site	Atom	s.o.f.	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}	Wyckoff position
Yb1	Yb	1	0.29760 (2)	0.19008 (2)	0	0.01566 (4)	24g
Yb2	Yb	0.005 (4)	0	0	0	0.02 (2)	2a
M1	Cd	1	0.34331 (2)	0.40651 (2)	0	0.01590 (5)	24g
M2a	Cd	0.60 (3)	0.5	0.4050 (3)	−0.2514 (2)	0.0337 (7)	24g
M2b	Cd	0.40 (3)	0.5	0.4149 (3)	−0.2663 (2)	0.0304 (4)	24g
M3a	Cd/Mg	0.58 (2)/0.050 (2)	0.3930 (2)	0.3072 (2)	−0.1528 (1)	0.0210 (2)	48h
M3b	Cd/Mg	0.34 (2)/0.029 (2)	0.3779 (6)	0.2971 (4)	−0.1563 (4)	0.0298 (7)	48h
M4a	Cd/Mg	0.486 (8)/0.066 (1)	0.1684 (2)	0.1684 (2)	0.1684 (2)	0.0284 (6)	16f
M4b	Cd/Mg	0.19 (2)/0.025 (3)	0.1472 (3)	0.1472 (3)	0.1472 (3)	0.020 (2)	16f
M4c	Cd/Mg	0.21 (2)/0.028 (2)	0.128 (1)	0.128 (1)	0.128 (1)	0.046 (3)	16f
M5	Cd/Mg	0.214 (4)/0.786 (4)	0.5	0.5	−0.09289 (8)	0.0331 (5)	12d
M6	Cd/Mg	0.102 (4)/0.898 (4)	0.1859 (1)	0.5	0	0.0224 (5)	12e
M7	Cd/Mg	0.0518 (5)/0.1140 (5)	0.0552 (6)	0.0554 (6)	0.0858 (4)	0.061 (2)	48h
M8	Cd	0.069 (3)	0.2677 (6)	0.2677 (6)	0.2677 (6)	0.063 (5)	16f

Table 5

Anisotropic atomic displacement parameters U_{ij} ($\text{\AA}^2$) of the $\text{Yb}_{13.3}\text{Cd}_{70.3}\text{Mg}_{16.5}$ 1/1 AP (sample 8) from refinement 2.

Site	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Yb1	0.01577 (6)	0.01490 (6)	0.01631 (6)	0.000	0.000	0.00140 (4)
M1	0.01412 (9)	0.01519 (9)	0.0184 (1)	0.000	0.000	0.00213 (7)
M2a	0.0222 (4)	0.0182 (7)	0.061 (2)	−0.0147 (9)	0.000	0.000
M2b	0.047 (2)	0.0170 (6)	0.028 (1)	−0.0018 (5)	0.000	0.000
M3a	0.0262 (4)	0.0198 (4)	0.0169 (3)	0.0015 (2)	0.0017 (3)	0.0059 (2)
M3b	0.043 (2)	0.0194 (7)	0.0267 (8)	0.0063 (5)	0.0169 (9)	0.0094 (9)
M4a	0.0284 (6)	0.0284 (6)	0.0284 (6)	0.0139 (6)	0.0139 (6)	0.0139 (6)
M4b	0.020 (2)	0.020 (2)	0.020 (2)	0.006 (1)	0.006 (1)	0.006 (1)
M4c	0.046 (3)	0.046 (3)	0.046 (3)	0.027 (4)	0.027 (4)	0.027 (4)
M5	0.0205 (6)	0.065 (1)	0.0139 (5)	0.000	0.000	0.000
M6	0.0130 (6)	0.0400 (1)	0.0144 (6)	0.000	0.000	0.000
M8	0.063 (5)	0.063 (5)	0.063 (5)	0.033 (5)	0.033 (5)	0.033 (5)

preferentially occupied by Mg. Two split positions of *M8* face each other across a high-symmetry position 1/4 1/4 1/4 with a split distance of about 0.97 (1) $\text{\AA}$ along a space diagonal. The corresponding electron-density isosurface is seen in Fig. 7(*d*). This site is a Cd preferential site with a low occupation probability of 0.138 (6).

The positional disorder observed in the present 1/1 AP at the cluster centre is comparable with what is named ‘type-I disorder’ in YbCd_6 (Pay Gómez & Lidin, 2003). The trigonal pyramid has lower symmetry than icosahedral symmetry and, in consequence, it will inevitably distort the surrounding shells. If one ignores the chemistry of the central trigonal pyramid, it can be regarded as a regular tetrahedron which was discussed in the binary 1/1 APs, and one can imagine that similar positional disorders occur owing to the orientational disorder of the tetrahedron in the present ternary 1/1 AP.

The tetrahedron can take one of the two distinct orientations as depicted in Fig. 7(*e*), and the atom at *M4* on the second dodecahedron shell will be pushed outwards or pulled inwards by the two different orientations. This push–pull mechanism gives rise to a large split atom, which can be seen as a strong elongation of the electron-density isosurface (Fig. 7*d*). Moreover, if the atom at *M4* is pushed outwards, it will push aside the atom at *M3*. Indeed, the split atom at *M3*

occurs so as to make the size of a triangle on the fourth icosidodecahedron shell larger. If we focus on the tetrahedra along one of the $\langle 111 \rangle$ directions, which correspond to the directions of the *c*-linkage, we find that there are three situations in terms of the arrangement between two adjacent tetrahedra, namely, push–push, pull–pull and push–pull (or pull–push). The first two configurations occur when the two adjacent tetrahedra take different orientations, and the last one occurs when they have the same orientation. The fractional atomic occupation at *M8* can be understood in the following way. In the case of push–push, there will be no room for an atom to occupy *M8*. In contrast, in the case of pull–pull, it is expected that an atom can occupy the position. By considering minor effects from other tetrahedra, it can be concluded that a full occupation of *M8* by an atom will never happen. Consequently, the positional disorders observed in the resulting structure are found to correlate with each other, regardless of dynamic origin or static origin. In other words, the disorders in this 1/1 AP mainly propagate through *c*-linkages. Thus, it is of great interest to compare the resulting atomic structures of the iQCs with that of the 1/1 AP in

terms of shell structures and their connections, *i.e.* *b*- and *c*-linkages.

5.4. Resulting atomic structures of i-Yb–Cd–Mg

Fig. 8 shows a projection of a thin slice ($40 \text{ \AA} \times 50 \text{ \AA} \times 1 \text{ \AA}$) perpendicular to a twofold axis including the centres of RTH clusters in the resulting atomic structure of $\text{i-Yb}_{15.5}\text{Cd}_{68.4}\text{Mg}_{16.1}$ (sample 3). The RTH cluster labelled by A, which has a local configuration of (12, 7, 5), connects with two neighbouring clusters, labelled by B and C, with *b*- and *c*-linkages, respectively, on this plane. The skewed rectangles, which correspond to the sections of dodecahedron shells, show heavy distortions along the *c*-linkages, accompanying a large split of the atomic site which is generated by OD d, along *c*-linkages. The skewed squares, which correspond to the sections of icosidodecahedron shells, also show split-atom sites, which are generated by OD f in Fig. 1(*b*), and the splits occur towards the dodecahedron sites generated by OD d in the adjoining RTH cluster. These characteristic distortions of the Tsai-type RTH cluster shells along *c*-linkages have also been observed not only for the parent $\text{i-YbCd}_{5.7}$ but also for the isostructural i-RCd ($R = \text{Gd, Dy, Tm}$) and $\text{i-ScZn}_{7.33}$ QCs (Yamada, Takakura, Euchner *et al.*, 2016; Yamada, Takakura, Kong *et al.*, 2016).

There are 18 different local RTH cluster configurations in the i-Yb–Cd–Mg QC model. Of these the most abundant one is the configuration of (12, 7, 5) (Takakura, 2008; Takakura & Strzalka, 2017). In contrast, every RTH cluster in the 1/1 AP has a unique local cluster configuration of (14, 6, 8). Although, this cluster configuration does not exist in the i-Yb–Cd–Mg QC model, it is of interest to compare the RTH cluster connection with *b*- and *c*-linkages at the atomic level in both structures. Fig. 9 juxtaposes the RTH cluster connections extracted from the i-Yb–Cd–Mg QC (sample 3) and 1/1 AP (sample 8). For the i-Yb–Cd–Mg QC, the dodecahedron shells in Figs. 9(a) and 9(c) come from the same RTH cluster having the local cluster configuration of (12, 7, 5). On the other hand, the icosidodecahedron shell in Fig. 9(a) comes from a neighbouring RTH cluster which has the configuration of (10, 6, 4), and that in Fig. 9(c) comes from another neighbouring RTH cluster which has the configuration of (12, 5, 7). Figs. 9(a) and 9(b) also show atoms on the vertices and mid-edges of a rhombus shared with RTH shells connected by a *b*-linkage, and Figs. 9(c) and 9(d) show atoms on the vertices and mid-

edges of an obtuse rhombohedron, *i.e.* the volume shared by two RTH shells connected by a *c*-linkage.

As seen in the figure, the atoms at the cluster centre tend to be ‘grouped’ in such a way that they resemble a tetrahedron in the iQC, whereas, in the 1/1 AP, they resemble a cube as discussed above. Heavy distortion of the dodecahedron shell in the iQC is clearly seen, which is induced by the central tetrahedron. In addition, the atomic sites on the dodecahedron and icosidodecahedron shells in the iQC were found to split in a manner similar to that found in the 1/1 AP: the split-atom positions on the dodecahedron shell (*d* for QC and *M4* for AP) occur along the *c*-linkage, and those on the icosidodecahedron shell (*f* and *M3*) occur towards the dodecahedron sites (*d* and *M4*) in the neighbour cluster. These common characteristic splits imply that the central tetrahedron in the i-Yb–Cd–Mg QCs induces the distortion of the surrounding shells by the same push–pull mechanism as seen in the 1/1 AP. It is thus considered that the positional disorder in the iQCs and 1/1 AP is induced essentially from the same origin, regardless of the quasi-periodic or periodic arrangement of the RTH clusters.

Recent studies on the ScZn₆ 1/1 AP, which is isostructural to the Yb–Cd–Mg 1/1 AP, by quasi-elastic neutron scattering and X-ray diffuse scattering experiments as well as atomic scale simulation revealed that (i) a Zn₄ tetrahedron at the cluster centre behaves as a ‘single molecule’ and reorients dynamically at ambient temperature; (ii) s.r.o. of the tetrahedra develops with decreasing temperature; (iii) the reorientation of the tetrahedra freezes below *T_c* (approximately 160 K) (Euchner *et al.*, 2012, 2013; Yamada *et al.*, 2013). Below *T_c*, the long-range orientational order of the tetrahedra establishes in an anti-parallel way along the [110] directions of the cubic

Figure 7

Shell structures, occupational and positional disorders in the resulting atomic structure of the Yb_{13.3}Cd_{70.3}Mg_{16.5} 1/1 AP (sample 8): (a) shell structures in the Tsai-type RTH cluster; electron-density isosurfaces at (b) *M7*, at (c) *M2* and *M5*, and at (d) *M3*, *M4*, and *M8*; (e) interpretation of the positional disorder at *M7* by a superposition of eight trigonal pyramids oriented along $\langle 111 \rangle$ directions. All the electron-density isosurfaces were drawn at the $7.5 \text{ e } \text{\AA}^{-3}$ level. The labels *M1*–*M8* and *Yb1* are the same those used in Table 4.

Figure 8

Projection of a thin slice ($40 \text{ \AA} \times 50 \text{ \AA} \times 1 \text{ \AA}$), perpendicular to the twofold axis, of the resulting atomic structure of i-Yb_{15.5}Cd_{68.4}Mg_{16.1} (sample 3). The octagons highlight the sections of RTH clusters. The RTH cluster *A*, which has a local configuration of (12, 7, 5), connects with two neighbouring RTH clusters, *B* and *C*, by *b*- and *c*-linkages, respectively. Atomic sites labelled by *d* and *f* are generated by the ODs labelled by *d* and *f* in Fig. 1, respectively.

lattice, accompanying a monoclinic lattice distortion (Tamura *et al.*, 2005; Ishimasa *et al.*, 2007; Yamada *et al.*, 2010, 2013). The dynamical disorder of the tetrahedron is accompanied by a large distortion of the surrounding cluster shells and thus results in 'dynamical flexibility' of the RTH cluster. Similar dynamical behaviour has been observed in the i-Sc-Zn-Mg and i-Sc-Zn-Ag QCs (Euchner *et al.*, 2013), which are isostructural to the i-Yb-Cd-Mg QCs, and such dynamical behaviour certainly plays an important role in the stabilization

Figure 9

Cluster connections in resulting atomic structures of i-Yb_{15.5}Cd_{68.4}Mg_{16.1} QC (sample 3) and the Yb_{13.3}Cd_{70.3}Mg_{16.5} 1/1 AP (sample 8). (a) *b*-linkage and (c) *c*-linkage in the iQC, and (b) *b*-linkage and (d) *c*-linkage in the 1/1 AP. Atomic sites labelled by *d* and *f* are generated by the ODs labelled by *d* and *f* in Fig. 1, respectively. The labels *M3*, *M4* are the same as those used in Table 4. For details, see the text.

Table 6

Coordinate number (CN) and number of Yb atoms in the CN, CN(Yb), in the atomic structures of the Yb-Cd-Mg iQC and 1/1 AP.

The labels for the OD of the iQC are the same as those used in Fig. 1. The labels for the atomic sites for the 1/1 AP are the same as in Table 4.

	OD	iQC		1/1 AP		
		CN	CN(Yb)	Site	CN	CN(Yb)
Dodecahedron	c	9.81	3.00	<i>M2</i>	11	3
	d	10.03	3.00	<i>M4</i>	14	3
Icosidodecahedron	f	10.53	2.78	<i>M3</i>	13	3
				<i>M5</i>	15	2
RTH	g	13.48	2.90	<i>M1</i>	12	3
	h	13.60	2.39	<i>M6</i>	12	2
	i	12.00	2.95			
	j	11.96	3.51			

mechanisms for the iQCs (de Boissieu, 2012). Since X-ray diffraction provides a spatial and temporal averaged structure, it is uncertain whether or not the origin of the orientational disorder is dynamical in the present i-Yb-Cd-Mg QCs and 1/1 AP, and this is one of the challenges for the future.

One of the intriguing outcomes revealed by the present structure analysis of i-Yb-Cd-Mg QCs may be that atomic site preferences exist for Mg when Cd atoms are substituted. To understand this characteristic structural feature, we further analysed the coordination number (CN) for the Cd/Mg sites. Table 6 shows the CN and number of Yb atoms in the CN, denoted as CN(Yb), for the atomic sites on the dodecahedron, icosidodecahedron and RTH shells in the i-Yb-Cd-Mg QCs and 1/1 AP. The CN and CN(Yb) for each atomic site in the i-Yb-Cd-Mg QCs were obtained by Voronoi tessellation to the atoms in a cube with a size of 80 Å × 80 Å × 80 Å, and they were then averaged over each group of atomic sites generated by the same OD. Taking into account the relative occupancies of Cd/Mg at each atomic site obtained by the structure analysis, it was found that the preferential sites for Mg have smaller CN(Yb) in both Yb-Cd-Mg iQCs and the 1/1 AP. Specifically, for the i-Yb-Cd-Mg QCs, the mid-edge site on the RTH shell, which is generated by OD *j* in Fig. 1(b), has the highest CN(Yb) equal to 3.5, and this site is occupied by pure Cd. In contrast, the vertex sites on the RTH shell, which are generated by OD *h*, have the lowest CN(Yb) equal to 2.4, and these sites are preferentially occupied by Mg. The positionally disordered sites of Cd on the dodecahedron and icosidodecahedron shells, which are generated by ODs *c* and *d* and OD *f*, respectively, have intermediate CN(Yb), ranging from 2.7 to 3.0. A similar tendency appears in the Yb-Mg-Cd 1/1 AP: the atomic sites having CN(Yb) equal to 3 are occupied by pure Cd, whereas those having CN(Yb) equal to 2 are occupied by a mix of Cd and Mg with the relative occupancy of Mg larger than 80%. The above results indicate that the local electronic structure plays a dominant role in the selective occupation of Mg. A quantitative estimation of the effects on the bonding nature caused by Mg substitution is of interest to understand the crystal chemistry of the i-Yb-Cd-Mg QCs as well as the 1/1 AP, and is another one of the challenges for the future.

6. Diffuse scattering

In §5 we mentioned the observation of the diffuse scattering intensities which have an arc shape on the twofold diffraction plane of the i-Yb–Cd–Mg QCs. To obtain details for the diffuse scattering phenomena, we have carried out synchrotron single-crystal XRD experiments for i-Yb_{15.5}Cd_{68.4}Mg_{16.1} (sample 3) on the CRISTAL beamline at the synchrotron SOLEIL.

Fig. 10 compares the reciprocal-space section reconstructed from the synchrotron data of i-Yb_{15.5}Cd_{68.4}Mg_{16.1}, perpendicular to the twofold axis, and its counterpart of the i-YbCd_{5.7} QC. The diffraction data for the i-YbCd_{5.7} QC were obtained on the BL22XU beamline at SPring-8. For i-Yb_{15.5}Cd_{68.4}Mg_{16.1}, arc diffuse scatterings are clearly visible; however, the centres of the arc diffuse scatterings, labelled by D and E for instance, cannot be indexed with the *P*-type icosahedral lattice, *i.e.* a sextet of integers. Instead, each position can be indexed with sextet half-integers, $\frac{33\frac{1}{2}33\frac{1}{2}}{222222}$ and $\frac{73\frac{3}{2}33\frac{3}{2}}{222222}$, respectively, using the indexing scheme proposed by Elser (1985). This indicates that they correspond to the reciprocal-lattice points of the *F*-type icosahedral lattice with a doubled icosahedral lattice constant of *P* types. In contrast, no arc diffuse scattering is observed for i-YbCd_{5.7}. [The diffuse scattering intensities that are seen nearby the strong Bragg

reflections are mainly due to those coming from phason fluctuations (de Boissieu *et al.*, 2002).] This demonstrates that some sort of s.r.o. is induced by the Mg substitution. In fact, the arc diffuse scatterings were found to be dependent on the Mg content. Fig. 11 juxtaposes the magnified views around the arc diffuse scatterings at $\frac{33\frac{1}{2}33\frac{1}{2}}{222222}$ on the twofold reciprocal-space sections of the i-Yb–Cd–Mg QC samples 2–6, obtained by laboratory XRD experiments. Although an absolute scale measurement is necessary to compare the diffuse intensities quantitatively, the following characteristic features are apparent: the arc diffuse scattering becomes the most intense and concentrates for the sample with 16.1 at.% of Mg (sample 3); the intensities at the central part of the arc become weaker when the radius of the arc becomes larger with increasing Mg content beyond 16.1 at.%. From the radius of the arc for sample 3, a correlation length of 68 Å can be deduced. For the diffuse scatterings at $\frac{73\frac{3}{2}33\frac{3}{2}}{222222}$, the intensities are too faint to observe the variation for the samples with Mg content greater than 16.1 at.%. This result indicates that some sort of s.r.o. develops mostly around the Mg content of 16.1 at.%.

In addition to the arc diffuse scatterings, two kinds of diffuse scattering phenomena were observed in the synchrotron data of i-Yb_{15.5}Cd_{68.4}Mg_{16.1} (sample 3): phason diffuse scattering and spot-shaped diffuse scattering. They can be recognized in Fig. 12 which shows a magnified view of a part of the first quadrant of Fig. 11. The phason diffuse scatterings are clearly visible, and they were found to be elongated along the threefold axes, similar to that observed in i-YbCd_{5.7} (de Boissieu *et al.*, 2002). The spot-shaped diffuse scatterings cannot be indexed with the *P*-type icosahedral lattice, yet they are indexed with the *F*-type icosahedral lattice as in the case of arc diffuse scatterings. For instance, the spot-shaped diffuse scatterings located at F, G and H are indexed as $\frac{71\frac{1}{2}11\frac{1}{2}}{222222}$, $\frac{33\frac{3}{2}33\frac{3}{2}}{222222}$ and $\frac{73\frac{5}{2}33\frac{5}{2}}{222222}$, respectively, with the *P*-type icosahedral lattice. Thus, this result demonstrates that s.r.o. of the *F*-type icosahedral superlattice develops in i-Yb_{15.5}Cd_{68.4}Mg_{16.1}. To investigate the evolution of the s.r.o. along with Mg content, a complete synchrotron data set is necessary for the other samples.

A simple model can be considered to understand the s.r.o. of the *F*-type icosahedral superlattice as follows. In the i-Yb–Cd–Mg QC model, the structure is described by a single Tsai-type RTH cluster and the clusters are located at the 12-fold packing vertices of the three-dimensional icosahedral lattice. It is known that the set of vertices can be divided into even-parity and odd-parity vertices (Henley, 1988). By assigning two distinguishable RTH clusters to the respective vertices, a structure model of *F*-type iQC with doubled icosahedral lattice constant with respect to the original *P*-type iQC can be obtained. Further, as two distinguishable RTH clusters, the following three simple cases can be considered. The first one is the case that RTH clusters at different parity vertices have different chemical order in terms of Mg occupations on the dodecahedron and/or icosidodecahedron shells. The second one is the case that a single Yb atom replaces the central tetrahedron of the RTH cluster located at either even-parity or odd-parity vertices. The last one is an orientational order of

Figure 10
Reciprocal-space sections perpendicular to a twofold axis reconstructed from the synchrotron single-crystal X-ray diffraction data for i-Yb_{15.5}Cd_{68.4}Mg_{16.1} QC (sample 3). The red open circles in the first quadrant indicate the locations of prominent arc diffuse scatterings. The reflections labelled by A, B and C, respectively, are indexed as $20\bar{1}01\bar{2}$, $21\bar{1}11\bar{1}$ and 201001 using Elser's six indexing scheme (Elser, 1985). The arc-shaped diffuse scatterings labelled by D and E are discussed in the text. The inset displayed in the third quadrant shows the intensity distribution observed in the i-YbCd_{5.7} QC.

Figure 11

Intensity distributions at $\frac{3\bar{1}1}{22} \frac{1331}{2222}$, corresponding to the position labelled by D in Fig. 3(a), on the twofold reciprocal layers reconstructed from the laboratory single-crystal X-ray diffraction data for the i-Yb-Cd-Mg QCs with Mg contents equal to (a) 6.4 at.% (sample 2), (b) 16.1 at.% (sample 3), (c) 25.3 at.% (sample 4), (d) 32.5 at.% (sample 5) and (e) 46.4 at.% (sample 6). Arc diffuse scatterings are indicated by white arrowheads.

the central tetrahedron of the RTH cluster, as in the case of the YbCd_6 and ScZn_6 1/1 APs, where the orientational order of the tetrahedron leads to the formation of superstructure at low temperature (Tamura *et al.*, 2002, 2005; Ishimasa *et al.*, 2007; Yamada *et al.*, 2013; Nishimoto *et al.*, 2013). With the above simple models, it may be possible to understand the spot-shaped diffuse scatterings, but the arc diffuse scatterings cannot be explained.

Localized diffuse scatterings, which have arc or spherical shell shapes in general, caused by s.r.o. within the iQC structure, have often been observed (Denoyer *et al.*, 1987; Goldman *et al.*, 1988; Gibbons & Kelton, 1993; Robertson & Moss, 1993). For instance, Denoyer *et al.* (1987) observed arc diffuse

X-ray scatterings for the first time from an i-Al-Li-Cu QC sample. Such localized diffuse scatterings were explained by a model based on bonded icosahedral clusters with the configuration of the 1/1 AP (Levine & Libbert, 1995). This so-called α -coordinated clusters model assumes that coherently oriented domains of the 1/1 AP are scattered within an iQC matrix. The arc diffuse scatterings observed in the present i-Yb-Cd-Mg QCs are similar to what was observed in the other iQCs, and may be explained in analogy with α -coordinated Tsai-type clusters.

However, the relation between the observed arc diffuse scatterings and s.r.o. of the *F*-type icosahedral superlattice is an open question. It is obvious that further investigations are necessary to reveal a correlation which produces the characteristic feature of diffuse scattering phenomena observed in the i-Yb-Cd-Mg QCs.

7. Summary

We have carried out a systematic structure refinement of the ternary i-Yb-Cd-Mg QCs with different Mg contents based on higher-dimensional crystallography by single-crystal X-ray diffraction, and made a comparison of occupational and positional disorder between the resulting structures and that of a 1/1 AP.

The average structures of the iQCs with Mg content up to about 46 at.% were found to be isostructural to the parent i-YbCd_{5.7}. On increasing the Mg content, Cd atoms at specific sites in the parent i-YbCd_{5.7} structure are replaced by Mg atoms in a systematic way. There are three types of atomic positions which show different behaviour in terms of Mg occupation: Mg preferential sites (type-I occupation) are located at the vertices of the RTH shell; Cd/Mg disorder sites (type-II occupation) are located on the vertices of decahedron and icosidodecahedron shells; Cd preferential sites (type-III occupation) are located on the edge-centres of the RTH shell. At low Mg contents, Mg atoms mainly replace Cd atoms located at type-I sites, and then the Mg occupancies there saturate at some early point. In contrast, Mg occupancies at type-II sites increase linearly with increasing Mg content. On the other hand, Cd atoms at type-III sites remain throughout the Mg substitutions. This selective occupation of Mg atoms in the Yb-Cd-Mg iQCs leads to the non-linear increase of the icosahedral lattice constant with increasing Mg content.

The 1/1 AP with the composition of $\text{Yb}_{13.30}\text{Cd}_{70.32}\text{Mg}_{16.48}$ was synthesized and its atomic structure determined by single-crystal X-ray diffraction. This ternary 1/1 AP turned out to be isostructural to the binary counterparts, such as YbCd_6 and ScZn_6 . Similar positional disorders originating from the orientational disorder of the central tetrahedron have been found. In addition, selective occupations of Mg atoms in terms of Tsai-type RTH cluster shells become apparent.

Figure 12

Magnified view of a part of the first quadrant of Fig. 10, which shows different types of diffuse scatterings. The red solid arrowheads indicate the locations of prominent spot-shaped diffuse scatterings. The white open arrowhead indicates an arc diffuse scattering. The red open arrowheads indicate the locations of diffuse scatterings due to phason fluctuations. The labels from A to E are the same as those in Fig. 10. The spot-shaped diffuse scatterings labelled by F, G and H are discussed in the text.

The positional disorder and the selective occupation of Mg atoms in terms of Tsai-type RTH clusters are common features of the iQCs and the corresponding 1/1 AP in the Yb–Cd–Mg system. The analysis of CN both in the atomic structures of the iQCs and in the 1/1 AP has shown that Mg occupation increases on the atomic site with a fewer number of Yb atoms in the CN. A quantitative estimation of the effects on the bonding nature caused by the Mg substitution would be necessary to understand the crystal chemistry of iQCs and the 1/1 AP in this system.

Finally, s.r.o. diffuse scatterings were observed for the iQCs at the positions corresponding to *F*-type icosahedral superlattice. This *F*-type s.r.o. was found to result from the Mg substitution, and simple *F*-type superstructure models with two distinguishable RTH clusters were suggested along the lines obtained from present structure analysis. Further investigations are necessary to reveal a correlation which produces the arc and spot-shaped diffuse scatterings observed in the Yb–Cd–Mg iQCs.

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