ELSEVIER
Journal of Alloys and Compounds xxx (2007) xxx–xxx
Journal of ALLOYS AND COMPOUNDS
www.elsevier.com/locate/jallcom

Crystal structure of the 2/1 cubic approximant $Ag_{42}In_{42}Yb_{16}$

M.R. Li [a,b,c,*], S. Hovmöller [c], J.L. Sun [c], X.D. Zou [c], K.H. Kuo [a,b,1]

[a] School of Materials Science and Engineering, Dalian University of Technology, 116024 Dalian, China
[b] Beijing Laboratory of Electron Microscopy, Institute of Physics, Chinese Academy of Sciences, 100080 Beijing, China
[c] Structural Chemistry, Stockholm University, SE-106 91 Stockholm, Sweden

Received 23 May 2007; received in revised form 19 October 2007; accepted 23 October 2007

Abstract

The crystal structure of the 2/1 cubic approximant $Ag_{42}In_{42}Yb_{16}$ was determined by single crystal X-ray diffraction. The structure model has the composition of $Ag_{40.42}In_{44.50}Yb_{15.08}$ with $a = 24.8687$ Å, space group $Pa\bar{3}$ (No. 205). Among the 14 independent Ag, 13 In, and 5 Yb sites, 6 Ag sites and 6 In sites are icosahedrally coordinated, whereas two sites (In13, Yb1) are Frank-Kasper polyhedrally coordinated. Four Yb sites (Yb2–5) are double pentagonal antiprisms. The basic structural unit can be described as a 102-atom pseudo-Bergman cluster with three successive shells, of which the second shell consists of a dodecahedron and an only nine-atom polyhedron that breaks icosahedral symmetry.

Keywords: Quasicrystals; X-ray diffraction

1. Introduction

Since an approximant has very close composition and similar structural unit to its quasicrystal, some local structures of quasicrystals are usually described by the structure of crystalline approximants. Of these, the Al-TM (TM = transition metal) class and the Al–Zn–Mg class of icosahedral quasicrystals are structurally related to their approximants α-Al–Mn–Si [1] and $(Al,Zn)_{49}Mg_{32}$ [2]. Their structures are considered as a packing of different icosahedral clusters, namely the Mackay icosahedron [3] cluster and the Bergman icosahedron [4] cluster, respectively. On the other hand, the icosahedral Al–Pd–Mn quasicrystal contains a cluster with interior breaking of icosahedral symmetry called a pseudo-Mackay icosahedron [5] which is characterized by an inner centered cubic core of nine atoms. This posed a very interesting question as to whether or not such an icosahedrally symmetry-breaking cluster can be involved in the formation of an icosahedral quasicrystal. However, what was observed in the icosahedral Al–Pd–Mn quasicrystals is not the sole case. In 2000, the first stable quasicrystal in Cd–Yb and Cd–Ca alloys was reported by Guo and Tsai et al. [6,7]. Their corresponding 1/1 cubic approximants $YbCd_6$ [8] and $CaCd_6$ [9] were then investigated by single crystal X-ray analysis as well as annular dark-field scanning transmission electron microscopy (ADF-STEM). Interestingly, these clusters in $YbCd_6$ and $CaCd_6$ consist of four Cd atoms forming a tetrahedron residing inside, which also breaks icosahedral symmetry. They are quite different from the well known Mackay and Bergman icosahedron clusters. The same clusters are also found in the 2/1 cubic approximants $M_{13}Cd_{76}$ (M = Ca, Yb) [10] of icosahedral Cd–Ca and Cd–Yb quasicrystals. In this paper, we investigated the 2/1 cubic approximant $Ag_{42}In_{42}Yb_{16}$ of Ag–In–Yb icosahedral quasicrystal [11]. Single crystal X-ray analysis indicates that it is isostructural to $Ca_{13}Cd_{76}$ (see Table 1). However, the detailed atomic structure is described here using a very different icosahedral cluster. It is another case of a symmetry breaking of the icosahedral symmetry of the cluster.

2. Experimental

An alloy sample of about 20 g with the nominal composition $Ag_{42}In_{42}Yb_{16}$ was prepared from the pure metals Ag (99.99%), In (99.99%) and Yb (99.9%) in a carbon crucible using a high-frequency induction furnace under an Ar atmosphere. The sample was first melted at 1100 °C and then re-melted at 800 °C followed by air-cooling. Grey octahedral single crystals were found inside the cast ingot and electron probe microanalysis (EPMA: JOEL JXA-8621MX) showed that their composition was $Ag_{41.7}In_{43.2}Yb_{15.1}$. A well-shaped crystal

* Corresponding author at: Structural Chemistry, Stockholm University, SE-106 91 Stockholm, Sweden. Tel.: +86 46 8 161104; fax: +86 46 8 152187.
E-mail address: mingrunl@fos.su.se (M.R. Li).
[1] 1923–2006.

0925-8388/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2007.10.096

Table 1
Atomic coordinates, occupancy, and isotropic displacement parameters of the 2/1 cubic approximant $Ag_{42}In_{42}Yb_{16}$ (this work) and $Ca_{13}Cd_{76}$

$Ag_{42}In_{42}Yb_{16}$							$Ca_{13}Cd_{76}$					
Atom	Occ.	Wyck.	*x*	*y*	*z*	U_{eq}	Atom	Occ.	Wyck.	*x*	*y*	*z*
Ag1	0.617	24d	0.3463(6)	0.5946(5)	0.1927(5)	0.0325(4)	Cdc	0.368	24d	0.3673(3)	0.5887(4)	0.1734(4)
Ag2	1	8c	0.2416(3)	0.2416(3)	0.2416(3)	0.0123(3)	Cd8	1	8c	0.2456(1)	0.2456(1)	0.2456(1)
Ag3	0.757	8c	0.0537(5)	0.4463(5)	0.5537(5)	0.024(6)	Cd2	0.825	8c	0.0565(1)	0.0435(9)	0.5565(1)
Ag3-	0.243	8c	0.0344(2)	0.4656(4)	0.5344(2)	0.017(2)	Cda	0.196	8c	0.0225(4)	0.4774(6)	0.5225(4)
							Cdb	0.196	8c	0.0889(4)	0.4111(6)	0.5889(4)
Ag4	1	24d	0.0011(2)	0.6551(2)	0.2861(2)	0.016(1)	Cd7	1	24d	0.00883(7)	0.65439(8)	0.28277(6)
Ag5	1	24d	0.3450(2)	0.5929(2)	0.3093(2)	0.0131(9)	Cd5	1	24d	0.34579(8)	0.59641(7)	0.30584(8)
Ag6	1	24d	0.2545(2)	0.5609(3)	0.2466(2)	0.020(2)	Cd4	1	24d	0.25670(2)	0.56438(8)	0.24658(8)
Ag7	1	24d	0.4963(3)	0.6555(2)	0.0980(2)	0.020(2)	Cd1	1	24d	0.49546(2)	0.65460(9)	0.09802(7)
Ag8	1	24d	0.4415(2)	0.7494(2)	0.0610(2)	0.012(1)	Cd3	1	24d	0.43960(8)	0.74875(8)	0.06052(8)
Ag9	1	8c	0.3454(2)	0.3454(2)	0.3454(2)	0.007(1)	Cd24	1	8c	0.34249(6)	0.34249(6)	0.34249(6)
Ag10	1	24d	0.2503(2)	0.4048(2)	0.3451(2)	0.0071(7)	Cd23	1	24d	0.25134(3)	0.40331(8)	0.34398(8)
Ag11	1	24d	0.2441(2)	0.2853(2)	0.3514(2)	0.0128(8)	Cd16	1	24d	0.23968(7)	0.28332(7)	0.35486(8)
Ag12	1	24d	0.1545(2)	0.5594(2)	0.4041(2)	0.0075(7)	Cd18	1	24d	0.15405(2)	0.55946(6)	0.40437(6)
Ag13	1	24d	0.1559(2)	0.4639(2)	0.3442(2)	0.0105(7)	Cd22	1	24d	0.15530(7)	0.46353(5)	0.34574(7)
Ag14	1	24d	0.4050(2)	0.3448(2)	0.4428(2)	0.0101(7)	Cd25	1	24d	0.40308(7)	0.34288(8)	0.44078(6)
In1	1	24d	0.0864(2)	0.4698(2)	0.4424(2)	0.0089(2)	Cd12	1	24d	0.08545(9)	0.47054(8)	0.44280(8)
In2	1	24d	0.1408(2)	0.4117(2)	0.1551(2)	0.0139(9)	Cd21	1	24d	0.14385(6)	0.41065(5)	0.15454(7)
In3	0.734	24d	0.1535(3)	0.2171(3)	0.3223(4)	0.026(3)	Cd6	1	24d	0.15359(9)	0.21618(7)	0.31911(9)
In3-	0.266	24d	0.1576(6)	0.2313(7)	0.3620(7)	0.016(5)						
In4	1	24d	0.1457(2)	0.5652(2)	0.2859(2)	0.0099(7)	Cd11	1	24d	0.14486(3)	0.56736(7)	0.28539(7)
In5	1	24d	0.0941(2)	0.4640(2)	0.2504(2)	0.0108(7)	Cd20	1	24d	0.09544(8)	0.46376(6)	0.25086(2)
In6	1	24d	0.0339(2)	0.5607(2)	0.0940(2)	0.0121(9)	Cd17	1	24d	0.03604(3)	0.55896(6)	0.09488(7)
In7	1	24d	0.1009(2)	0.6558(2)	0.3523(2)	0.0139(8)	Cd13	1	24d	0.10130(5)	0.65445(7)	0.35442(6)
In8	0.902	24d	0.2162(2)	0.4511(2)	0.2400(2)	0.009(1)	Cd14	1	24d	0.21466(8)	0.45353(7)	0.24085(8)
In9	0.886	24d	0.2169(2)	0.4510(2)	0.0738(2)	0.015(2)	Cd19	1	24d	0.21509(7)	0.45153(7)	0.06877(7)
In10	0.626	24d	0.4782(8)	0.3361(6)	0.5281(4)	0.010(4)	Cd26	1	24d	0.46284(7)	0.34377(2)	0.53354(7)
In10-	0.374	24d	0.4565(1)	0.3474(5)	0.5376(7)	0.021(6)						
In11	1	24d	0.2302(2)	0.4709(2)	0.4480(2)	0.0111(8)	Cd15	1	24d	0.23029(8)	0.47175(8)	0.44906(8)
In12	1	24d	0.4219(2)	0.5278(2)	0.3627(2)	0.0185(1)	Cd9	1	24d	0.42226(4)	0.52621(8)	0.36021(7)
In13	1	24d	0.2640(2)	0.5267(2)	0.3581(2)	0.0171(9)	Cd10	1	24d	0.26481(8)	0.52788(8)	0.35588(8)
Yb1	1	8c	0.46113(9)	0.46113(9)	0.46113(9)	0.0015(6)	Ca5	1	8c	0.4594(2)	0.4594(2)	0.4594(2)
Yb2	1	24d	0.15803(9)	0.54105(9)	0.15435(9)	0.0043(4)	Ca1	1	24d	0.158009	0.539373	0.153097
Yb3	1	24d	0.15306(9)	0.33949(9)	0.26892(9)	0.0047(4)	Ca3	1	24d	0.1545(2)	0.3411(2)	0.2689(1)
Yb4	1	24d	0.03026(3)	0.53913(8)	0.34531(9)	0.0025(4)	Ca2	1	24d	0.0315(2)	0.5404(2)	0.3462(2)
Yb5	1	24d	0.27245(9)	0.3468(1)	0.46486(9)	0.0057(4)	Ca4	1	24d	0.2693(2)	0.3453(2)	0.4667(2)
							Cde	0.322	24d	0.1152(4)	0.1483(4)	0.2109(4)
							Cdf	0.279	24d	0.1594(5)	0.2288(4)	0.1652(4)

(0.08 mm × 0.05 mm × 0.05 mm) was selected and used for single crystal X-ray diffraction.

Single crystal X-ray diffraction data was collected on a Bruker Smart CCD diffractometer equipped with a graphite monochromator using Mo Kα ($\lambda = 0.71069$ Å). Lattice parameters, $a = 24.8687$ Å, were obtained and refined from 7498 good reflections with θ in the range 4.4–30.5°. A total of 129 609 reflections, within the range $-29 \le h \le 37$, $-27 \le k \le 37$, $-38 \le l \le 38$, were collected. Nine thousand nine hundred and fifty-nine of these were unique. The absorption correction was done by empirical methods [12]. The estimated minimum and maximum transmission factors were 0.6792 and 0.7796.

3. Structure determination

The structure of the cubic $Ag_{42}In_{42}Yb_{16}$ phase was determined by direct methods using SHELXS-97 [13] and refined by SHELXL-97 [14]. The intensity distribution of the X-ray diffraction patterns implies that the Laue class of the cubic $Ag_{42}In_{42}Yb_{16}$, is $m\bar{3}$. The reflection conditions $0\,k\,l$: $k = 2n$ and $h\,0\,0$: $h = 2n$ proved the space group to be $Pa\bar{3}$ (No. 205). Due to the beam stop, the intensities of the reflections at the low angle range are not very good, so only the reflections with 5.1 Å < d-value < 0.85 Å were used for the final structure refinement. All positions with large electron density were assigned as Yb atoms. Positions with lower electron density were assigned as Ag or In. Since Ag^{+} and In^{3+} atoms have the same number of electrons, the element-type at this kind of positions was determined based on its coordination number and the averaged distance to its co-coordinated atoms. According to these rules, all sites with coordination number (CN) over 12 were considered to be In, while those less than 12 were taken as Ag. For the 12 sites with CN12, they are separated using the averaged distances. Those bigger than 3.09 Å were considered to be In, while those smaller than 3.09 Å were taken as Ag. The averaged distance of In5 is 3.09 Å. In order to achieve agreement between our experimental (EPMA) and calculated compositions, we assigned this site as In. In summary, the sites with CN12 are distributed as 6 In and 6 Ag. Totally, there are 5 Yb, 14 Ag and 13 In-

independent sites. All sites are in general 24-fold positions, except for Ag2, Ag3 and Yb1, which are in 8c. Several Ag and In sites had relatively large atomic displacement parameters. To reduce them into normal values, they were treated as disordered (Ag3/Ag3-, In3/In3- and In10/In10-) or partially occupied (Ag1, In8 and In9) (see Table 1). Finally, the isotropic displacement parameters U_{eq} were in the range of 0.007–0.020 Å^2 for most Ag and In and 0.001–0.006 Å^2 for Yb atoms. The largest isotropic displacement parameter was 0.0325 Å^2 for Ag1 with occupancy of only 0.617. The final refinement based on F_o^2 led to $R = 0.0523$, $wR2 = 0.1551$ for 6881 unique reflections observed with $F_o > 4\sigma(F_o)$, $R = 0.0934$, $wR2 = 0.1788$ for all the 9959 unique reflections. The calculated composition of $Ag_{42}In_{42}Yb_{16}$ from this structure model is $Ag_{40.42}In_{44.50}Yb_{15.08}$, which is very close to that from the EPMA analysis.

4. Structure description

When comparing $Ag_{42}In_{42}Yb_{16}$ to the 2/1 cubic approximant $Ca_{13}Cd_{76}$ (see Table 1), most fractional atomic coordinates agree to within 0.01. Thus, we consider $Ag_{42}In_{42}Yb_{16}$ as isostructural to $Ca_{13}Cd_{76}$. Compared with the structure of $Ca_{13}Cd_{76}$, there are only two positions missing in our structure, Cde and Cdf. These two sites are heavily disordered in $Ca_{13}Cd_{76}$ with occupancies of 32.2% and 27.9%, respectively. They have very short distances to other atoms, such as 1.229 Å for Cde–Cdc, 1.375Å for Cde–Cdf and 2.537 Å for Cdf–Cd5.

4.1. Coordination polyhedra

The coordination polyhedra are very clear for all 32 unique atoms. All atoms in the first shell are closer than 4.0 Å to the central atom. In nearly every case there is a big jump in distances; the atoms in the first sphere are always in the range 2.7–3.5 Å, except for four cases where Yb is involved in the first shell and the distances are larger (3.6–3.8 Å). Coordination polyhedra of all the 32 independent atoms are shown in Fig. 1. The corresponding coordination number (CN), the range of distances and averaged distances are listed in Table 2. Among the 14 Ag and 13 In sites, 6Ag (Fig. 1(I)i–n) and 6In (Fig. 1(II)a–f) sites are icosahedrally coordinated. The In13 site is a CN15 deltahedron (enclosed by 26 triangular faces and 15 vertices) described by Kasper in the Frank–Kasper phases [15,16]. Four out of the five Yb atoms have CN16. Only Yb5 has CN17. The

Table 2
Coordination number (CN), the averaged distances (d_{ave}), the range of distances (d_{min} and d_{max}), and the type of polyhedron of the 2/1cubic approximant $Ag_{42}In_{42}Yb_{16}$

Atom	CN				d_{ave}	d_{min}	d_{max}	Type of polyhedron
	Ag	In	Yb	Total				
Ag1	7	0	1	8	3.01(20)	2.794(14)	3.818(12)	–
Ag2	3	3	3	9	3.11(16)	2.951(11)	3.356(3)	–
Ag3	3	3	3	9	3.09(13)	2.956(12)	3.287(3)	–
Ag4	5	2	3	10	3.04(17)	2.865(7)	3.384(6)	–
Ag5	3	4	3	10	3.02(19)	2.818(14)	3.327(5)	–
Ag6	3	4	3	10	3.03(20)	2.794(14)	3.380(6)	–
Ag7	4	3	3	10	3.02(19)	2.838(7)	3.361(6)	–
Ag8	4	4	3	11	3.05(18)	2.857(7)	3.346(5)	–
Ag9	9	0	3	12	3.02(23)	2.793(5)	3.483(3)	ICO
Ag10	5	4	3	12	3.06(17)	2.770(6)	3.463(5)	ICO
Ag11	6	3	3	12	3.08(13)	2.882(13)	3.354(6)	ICO
Ag12	2	7	3	12	3.08(18)	2.799(6)	3.444(5)	ICO
Ag13	3	7	2	12	3.06(22)	2.770(6)	3.631(5)	ICO
Ag14	4	5	3	12	3.08(14)	2.773(11)	3.346(5)	ICO
In1	5	4	3	12	3.11(15)	2.838(7)	3.359(5)	ICO
In2	1	8	3	12	3.10(16)	2.818(14)	3.363(5)	ICO
In3	4	5	3	12	3.11(13)	2.882(9)	3.324(8)	ICO
In4	3	6	3	12	3.13(22)	2.869(13)	3.513(5)	ICO
In5	1	8	3	12	3.09(19)	2.739(13)	3.452(5)	ICO
In6	0	8	4	12	3.11(19)	2.712(12)	3.463(5)	ICO
In7	6	4	3	13	3.14(16)	2.884(8)	3.516(5)	–
In8	5	5	3	13	3.17(19)	2.901(8)	3.519(5)	–
In9	2	8	3	13	3.14(20)	2.820(7)	3.510(5)	–
In10	2	9	2	13	3.13(27)	2.712(12)	3.619(11)	–
In11	5	7	2	14	3.15(17)	2.748(7)	3.516(5)	–
In12	4	7	3	14	3.19(18)	2.871(8)	3.502(6)	–
In13	6	7	2	15	3.19(20)	2.748(7)	3.519(5)	Frank–Kasper CN15 polyhedron
Yb1	3	12	1	16	3.32(11)	3.097(6)	3.527(5)	Frank–Kasper CN16 polyhedron
Yb2	4	12	0	16	3.36(6)	3.228(5)	3.619(5)	Monocapped, double pentagonal antiprism
Yb3	8	8	0	16	3.36(7)	3.248(5)	3.610(5)	Monocapped, double pentagonal antiprism
Yb4	7	9	0	16	3.36(6)	3.278(5)	3.631(5)	Monocapped, double pentagonal antiprism
Yb5	12	5	0	17	3.38(7)	3.284(6)	3.818(5)	Double capped, double pentagonal antiprism

The e.s.d.s of d_{max} are smaller than those of the d_{min} because they usually involve an Yb atom and those have much smaller e.s.d.s than Ag and In.

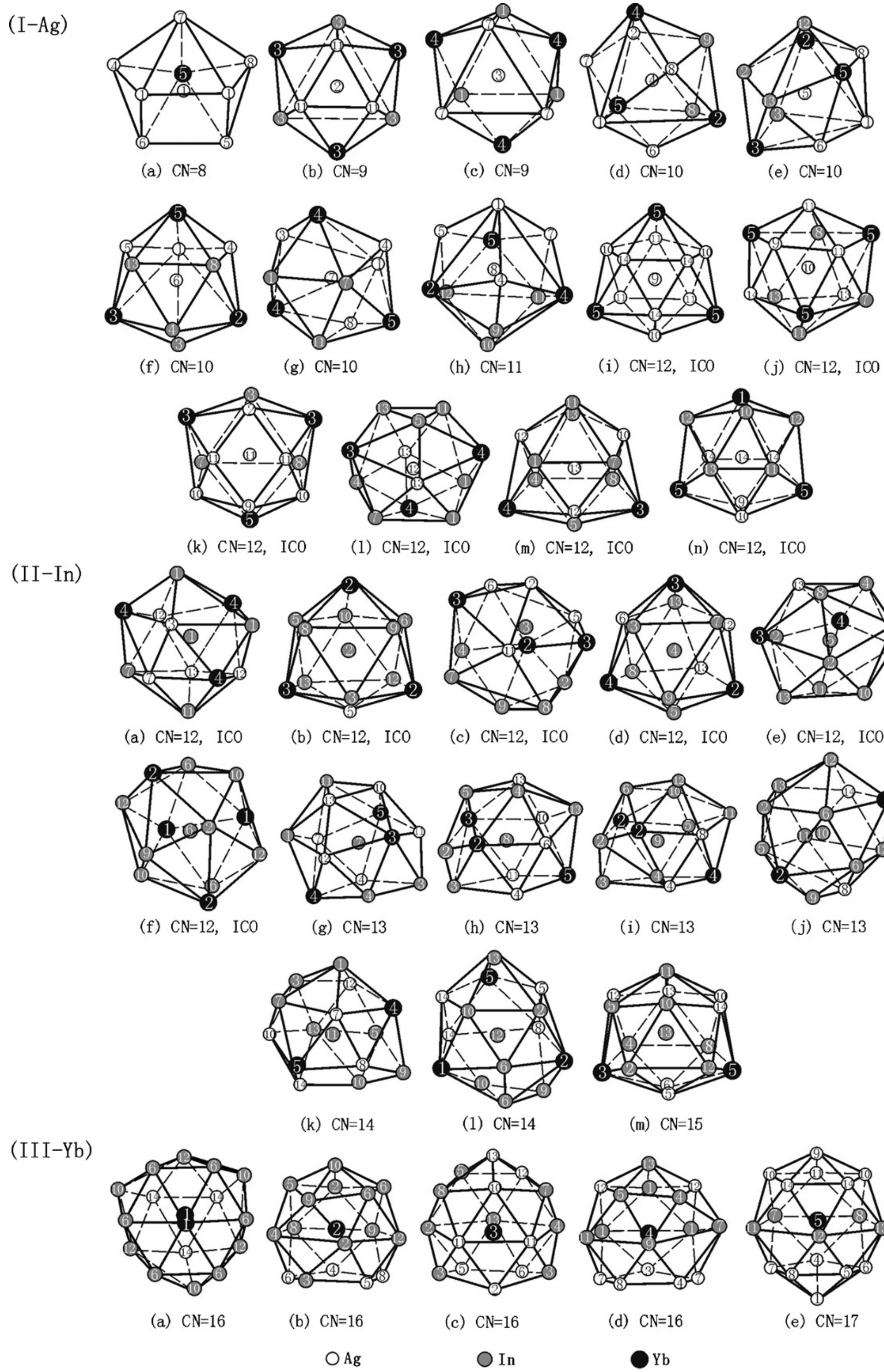

Fig. 1. Coordination polyhedra in $Ag_{42}In_{42}Yb_{16}$. Among the 14 Ag and 13 In sites, 6 Ag (I(i–n)) and 6 In (II(a–f)) sites are icosahedrally coordinated. With the increase of atomic radius from Ag (1.44 Å), In (1.67 Å) to Yb (1.94 Å), the coordination number increases from 8–12 over 12–15 to 16–17.

Yb5 polyhedron with CN17 is a double capped, double pentagonal antiprism, whereas Yb2–4 polyhedra with CN16 are monocapped, double pentagonal antiprisms. However, the Yb1 site, surrounded by three Ag atoms, 12 In atoms and one Yb1 atom, is a Frank–Kasper CN16 deltahedron (enclosed by 28 triangular faces and 16 vertices) [15,16]. Yb2–5 polyhedra show nearly perfect fivefold symmetry seen from the $\langle \tau\, 1\, 0\rangle$ direction, while the Yb1 Frank–Kasper CN16 polyhedron displays very strict threefold symmetry from the projecting [1 1 1] direction. With the increase of atomic radius from Ag (1.44 Å) over In (1.67 Å) to Yb (1.94 Å), the coordination number generally increases from 8–12, 12–15 to 16–17 (see Table 2).

The average distances (d_{ave}) increase slightly with coordination number CN, as shown in Fig. 2. In addition, the averaged distances increase from Ag over In to Yb atoms (3.01–3.11 Å for Ag, 3.09–3.19 Å for In, 3.32–3.38 Å for Yb, see Table 2 and Fig. 2). All Ag and In sites are surrounded by 2–4 Yb atoms, mostly three. In contrast, all Yb atoms, except for Yb1, are surrounded only by Ag and In atoms. It seems that the larger Yb atom tries to avoid direct contact with other Yb atoms. The same structural rule was also observed in the Zn–Mg–RE alloy system, such as μ_7-Zn–Mg–Sm [17] and (Zn, Mg)$_4$Ho/Er [18]. The distances from the center to a vertex in a polyhedron in $Ag_{42}In_{42}Yb_{16}$ are within the ranges: Ag–Ag = 2.770–3.296 Å, Ag–In = 2.838–3.265 Å, In–In = 2.712–3.516 Å, Ag–Yb = 3.244–3.609 Å, In–Yb = 3.097–3.818 Å. The distance of the only Yb–Yb pair is 3.348 Å.

4.2. Three-shell 102-atom icosahedral cluster

Three successive shells of a basic building block of $Ag_{42}In_{42}Yb_{16}$ are shown along the [1 1 1] projection in Fig. 3. The central Ag9 atom located on the $\langle 1\, 1\, 1\rangle$ diagonal at (0.345, 0.345, 0.345) is surrounded by 12 atoms (9Ag + 3Yb) forming an icosahedron (ICO). It is noteworthy that in this first ICO shell, Ag atoms have distances of 2.792–2.958 Å from the central Ag atom while the large Yb5 atoms in this icosahedron shell are

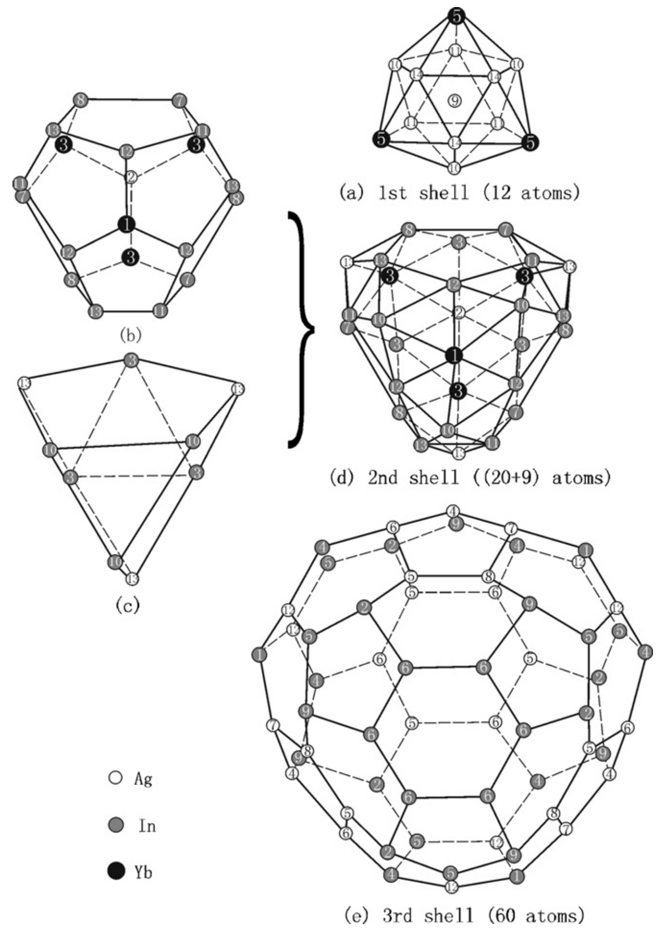

Fig. 3. Three-shell 102-atom pseudo-Bergman cluster in $Ag_{42}In_{42}Yb_{16}$: (a) the first shell consists of nine Ag and three Yb atoms, forming a distorted icosahedron with an Ag9 center; (b) 20-atom dodecahedron; (c) nine-atom polyhedron breaking icosahedral symmetry; (d) the second shell includes a 20-atom dodecahedron (b) and a nine-atom polyhedron (c); (e) the third shell consists of 27 Ag atoms and 33 In atoms, forming a truncated icosahedron. (a) is seen exactly along $\langle 1\, 1\, 1\rangle$ while the others are tilted a little forward for clarity.

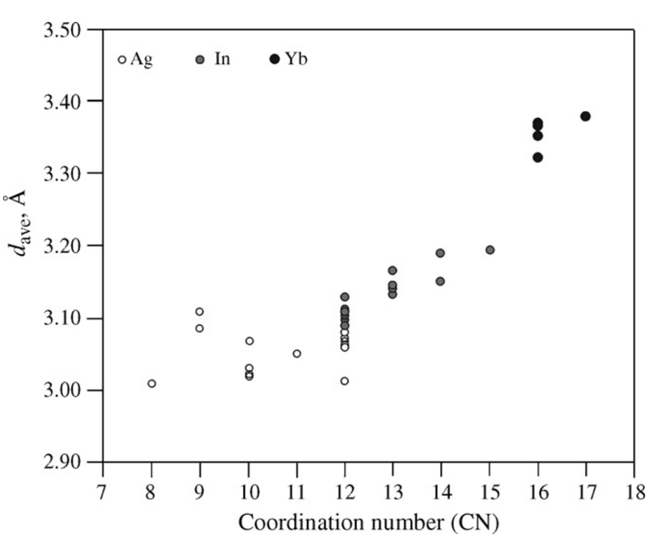

Fig. 2. Plots of the average distance (d_{ave}) vs. the coordination number in the 2/1 cubic approximant $Ag_{42}In_{42}Yb_{16}$.

0.5–0.6 Å further away from the central Ag atom. Therefore, it is not a regular icosahedron shell. The second shell (see Fig. 3(d)) having a radius of 5.2–5.8 Å can be divided into two parts, a pentagonal dodecahedron (see Fig. 3(b)) including 20 atoms (1 Ag + 15 In + 4 Yb) located at a radius of 5.2 Å and an irregular polyhedron consisting of only nine atoms (3 Ag + 6 In) located at a radius of 5.8 Å. Each atom in the second part is situated above the centers of the pentagonal faces of the dodecahedron, except for the three symmetric In8–In7–In11–In12–In13 faces (see Fig. 3(a) and (d)). The reason for this is that the large Yb5 atoms in the first ICO shell are so close to the center of the In8–In7–In11–In12–In13 pentagon (only 0.2 Å) that there is not enough room to accommodate any other atoms above these pentagonal faces. Atoms on this face will cause a short distance (2.3 Å) between the Yb5 atom and the second shell. The third shell (see Fig. 3(e)), having a radius of 6.6–7.8 Å, consists of 27 Ag and 33 In atoms, forming a somewhat distorted soccer ball (truncated icosahedron). The total number of atoms of these three shells (including the center atom) are 102 (1 + 12 + (20 + 9) + 60) atoms. Unfortunately it is not possible to compare these structures to $Al_{17}Zn_{37}Mg_{46}$ [20], since no atomic co-ordinates were published for that structure yet.

4.3. Polyhedra connecting along the direction close to the ⟨τ 1 0⟩ direction

Fivefold rotational symmetry is associated with the golden number $\tau = (1+\sqrt{5})/2$ or $\cos 72^\circ = (\tau - 1)/2$. Elser and Henley [1] used the rational ratio of two successive Fibonacci numbers F_{n+1}/F_n as an approximation to substitute for the irrational τ, to obtain the crystalline approximant of an icosahedral quasicrystal. The pseudo-fivefold axes of the cubic approximant is along a direction close to the $\langle \tau\, 1\, 0\rangle$ direction of the icosahedral quasicrystal. Two chains of interpenetrating polyhedra are found close to the $[\tau\, 1\, 0]$, and $[\tau\, \bar{1}\, 0]$ directions, as seen in Fig. 4. In one of these chains, there are three penetrating icosahedra centered at Ag13, Ag10, and Ag9, and one Yb5 double capped, double pentagonal antiprism (see Fig. 4(a)). The hatched pentagonal faces with their fivefold axis along the direction to the $\langle \tau\, 1\, 0\rangle$ direction are shared by two interpenetrated polyhedra. Similarly, four penetrating icosahedra, In3, Ag11, Ag9, and Ag14 ICO, together with the CN13 In10 polyhedron form another chain of polyhedra (see Fig. 4(b)). These 12 hatched pentagons designated 1st, 2nd, and 3rd, can also be identical in the three successive shells of the previously presented Bergman cluster (see Fig. 3). Since the Bergman cluster in Fig. 3 is centered on the threefold axis, all the pentagons in the Bergman cluster can be divided into three groups according to the symmetry. Totally, there are 36 pentagons with their fivefold axes along the direction close to the $\langle \tau\, 1\, 0\rangle$ direction in one Bergman cluster. All of the polyhedron chains in this 102-atom Bergman cluster are expected to show pseudo fivefold symmetry along the direction close to $\langle \tau\, 1\, 0\rangle$ direction. Recently, Deng and Kuo [19] investigated the structure of the 2/1 cubic approximant $Ag_{42}In_{45}Ca_{13}$ by means of selected-area electron diffraction. Its $[\tau\, 1\, 0]$ electron diffraction pattern consisting of diffraction spots of the [2 1 0], [3 2 0], and [5 3 0] axes, etc., exhibits a strong pseudo-fivefold symmetry. This result agrees very well with the structure of $Ag_{42}In_{42}Yb_{16}$.

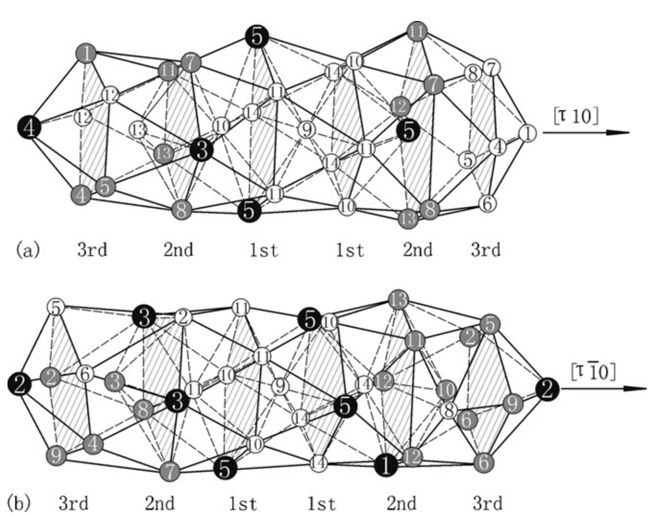

Fig. 4. Polyhedra interpenetrating along the direction close to the $\langle \tau\, 1\, 0\rangle$ direction in $Ag_{42}In_{42}Yb_{16}$.

Table 3
Three 2/1 cubic approximants related to icosahdral quasicrystal with different icosohedral clusters

Compositions	Parameter (Å)	Space group	Bergman cluster
$Al_{17}Zn_{37}Mg_{46}$ [20]	23.1	$Pa\bar{3}$	0 + 12 + 20 + 12 + 60
$Ca_{13}Cd_{76}$ [10,21]	25.339	$Pa\bar{3}$	0 + 4 + 20 + 12 + 30
$Ag_{42}In_{42}Yb_{16}$	24.8687	$Pa\bar{3}$	1 + 12 + (20 + 9) + 60

5. Discussion

Approximants play an important role in the study of the atomic structure of quasicrystals, because their unit cells display almost the same local atomic structure as the true quasicrystals. In order to understand the local structure characteristic of icosahedral quasicrystals, it is necessary to compare the detailed atomic distribution in successive shells of different basic building blocks in their approximants. Here, we list three 2/1 approximants with lattice parameters between 23 and 25 Å, space group $Pa\bar{3}$ (see Table 3). All of their crystal structures have been determined by single crystal X-ray diffraction analysis.

The 2/1 cubic approximant $Al_{17}Zn_{37}Mg_{46}$ [20], contains a complete four-shell Bergman cluster where its center void, the first to the fourth shell, each having icosahedral symmetry, correspond to an inner icosahedron, a dodecahedron, an outer icosahedron, and a truncated icosahedron. The total atoms of this Bergman cluster are 104 (0 + 12 + 20 + 12 + 60) atoms. For the present 2/1 cubic approximant $Ag_{42}In_{42}Yb_{16}$, as has been discussed in Fig. 3, its second shell includes a 20-atom dodecahedron and an only nine-atom polyhedron which breaks icosahedral symmetry. In contrast to the third shell of Bergman cluster in $Al_{17}Zn_{37}Mg_{46}$, the polyhedron in Fig. 3(c) can be described as an outer icosahedron with its three pentagon caps cut. Obviously, it is different from the usual 105-atom (with an atom at the center) or 104-atom (without central atom) Bergman cluster, such as the cluster of $Al_{17}Zn_{37}Mg_{46}$. In this regard, the 102-atom cluster of $Ag_{42}In_{42}Yb_{16}$ can be named a pseudo-Bergman cluster. In a unit cell, eight such pseudo-Bergman clusters or their extended clusters are packed closely and form the skeleton of the $Ag_{42}In_{42}Yb_{16}$. This kind of stack is frequently present in crystal structures of cubic approximants, including $Al_{17}Zn_{37}Mg_{46}$.

Since $Ag_{42}In_{42}Yb_{16}$ is isostructural to $Ca_{13}Cd_{76}$, it is expected that the latter should also be built up by pseudo-Bergman clusters. However, the atomic structure of the $Ca_{13}Cd_{76}$ was described by Gomez et al. using a very different icosohedral cluster [10,22]. Its first shell consists of four Cd atoms forming a tetrahedron residing inside, which also breaks icosahedral symmetry, the second to the fourth shell, each having 20 Cd, 12 Ca, and 30 Cd atoms, forming a dodecahedron, icosahedron, and icosidodecahedron, respectively. Eight 66-atom clusters that extend to a triacontahedron together form a cubic close-packed arrangement of partially interpenetrating triacontahedra. Obviously, their 66-atom (4 + 20 + 12 + 30) cluster is neither a Bergman nor a Mackay icosohedral cluster type. The reason why $Ag_{42}In_{42}Yb_{16}$ and $Ca_{13}Cd_{76}$ are described by very different icosahedral clusters is only that different cluster centers were chosen in these two cases. The former centered at 8c (0.345, 0.345, 0.345), while the latter at another 8c site (0.153, 0.153, 0.153). Thus, the structures of these types of 2/1 cubic approximants can be described by either 102-atom pesudo-Bergman clusters or 66-atom icosahedral clusters. Thus, these two types of icosahedral clusters coexist in the 2/1 cubic approximants $Ag_{42}In_{42}Yb_{16}$ and $Ca_{13}Cd_{76}$, indicating that they may also coexist in their icosahedral quasicrystals. This shows us not only a new structure characteristic in quasicrystal structure, but also a new approach to describe the quasicrystal structure.

6. Conclusion

In this paper, the 2/1 cubic approximant $Ag_{42}In_{42}Yb_{16}$, isostructural to $Ca_{13}Cd_{76}$, was described using a 102-atom pseudo-Bergman cluster with three successive shells, of which the second shell consists of a dodecahedron and an only nine-atom polyhedron that breaks icosahedral symmetry. It differs from the usual 105-atom (with a center) or 104-atom (without a center) Bergman cluster whose second shell consists of a dodecahedron and a 12-atom icosahedron. This is possibly owing to the presence of relatively large Yb atoms in the first ICO shell in the cubic 2/1 cubic approximant $Ag_{42}In_{42}Yb_{16}$. Furthermore, the relationship between the pseudo-Bergman cluster and the 66-atom cluster was discussed. They both occur in the unit cell, but with different cluster centers, and any of them can be used to describe the crystal structure independently.

Acknowledgements

The author specially thanks Prof. W. Sun, Prof. A.P. Tsai and Dr. C.P. Gomez for fruitful discussions and constructive suggestions. The crystals used in this work were made in the State Key Laboratory for Advanced Metals and Materials of University of Science and Technology (Beijing). The authors are grateful for the help of Prof. X.D. Hui providing experimental facilities. We would also like to thank Dr. G.W. Li of China University of Geosciences (Beijing) for the assistance in X-ray data collection. This study is supported by the National Natural Science Foundation of China through a grant (No. 10074073), the Swedish Research Council (VR) and the Royal Swedish Academy of Sciences.

References

[1] V. Elser, C.L. Henley, Phys. Rev. Lett. 55 (1985) 2883.
[2] C.L. Henley, V. Elser, Phil. Mag. Lett. 53 (1986) L59.
[3] A.L. Mackay, Acta Cryst. 15 (1962) 916.
[4] G. Bergman, J.L.T. Waugh, L. Pauling, Acta Cryst. 10 (1957) 254.
[5] M. Boudard, M.D. Boissieu, C. Janot, G. Heger, C. Beeli, H.-U. Nissen, H. Vincent, R. Ibberson, M. Audier, J.M. Dubois, J. Phys.: Condens. Matter 4 (1992) 10149.
[6] A.P. Tsai, J.Q. Guo, E. Abe, H. Takakura, T.J. Sato, Nature 408 (2000) 537.
[7] J.Q. Guo, A. Abe, A.P. Tsai, Phys. Rev. B 62 (2000) R14605.
[8] H. Takakura, J.Q. Guo, A.P. Tsai, Phil. Mag. Lett. 81 (2001) 411.
[9] E. Abe, A.P. Tsai, J. Non-Cryst. Solids 334/335 (2004) 190.
[10] C.P. Gomez, S. Lidin, Angew. Chem. Int. Ed. 21 (2001) 4037.
[11] J.Q. Guo, A.P. Tsai, Phil. Mag. Lett. 82 (2002) 349.
[12] A.C.T. North, D.C. Philips, F.S. Mathews, Acta Cryst. A 24 (1968) 351.
[13] G.M. Sheldrick, SHELXS-97, Program zur Verfeinerung von Kristallstrukturen Göttingen, University of Goettingen, Germany, 97-102.(1997).
[14] G.M. Sheldrick, T.R. Schneider, Macromol. Crystallogr. Pt B (1997) 319.
[15] J.S. Kasper, Theory of Alloy Phases, American Society of Metals, Cleveland, OH, 1956, pp. 264–278.
[16] F.C. Frank, J.S. Kasper, Acta Cryst. 11 (1958) 184;
F.C. Frank, J.S. Kasper, Acta Cryst. 12 (1959) 483.
[17] K. Sugiyama, K. Yasuda, Y. Horikawa, T. Ohsuna, K. Hiraga, J. Alloys Compd. 285 (1997) 172.
[18] M.R. Li, D.W. Deng, K.H. Kuo, J. Alloys Compd. 414 (2006) 66.
[19] B.B. Deng, K.H. Kuo, J. Alloys Compd. 366 (2004) L1.
[20] K. Sugiyama, W. Sun, K. Hiraga, J. Alloys Compd. 342 (2002) 139.
[21] C.P. Gomez, S. Lidin, Phys. Rev. B 68 (2003) 024203.
[22] H. Takakura, C.P. Gomez, A. Yamamoto, M.D. Boissieu, A.P. Tsai, Nat. Mater. 6 (2007) 58.

Please cite this article in press as: M.R. Li, et al., J. Alloys Compd. (2007), doi:10.1016/j.jallcom.2007.10.096