

# Materials Characterization

## Quasicrystalline clusters transformed from C14-MgZn<sub>2</sub> nanoprecipitates in Al alloys --Manuscript Draft--

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<b>Corresponding Author:</b>	Kai Li Central South University Changsha, CHINA
<b>First Author:</b>	Tong Yang
<b>Order of Authors:</b>	Tong Yang Yi Kong Kai Li Qiang Lu Yucheng Wang Yong Du Dominique Schryvers
<b>Abstract:</b>	Ultrafine faulty C14-MgZn <sub>2</sub> Laves phase precipitates containing quasicrystalline clusters and demonstrating the formation of binary quasicrystalline precipitates with Penrose-like random-tiling were observed in the over-aged FCC matrix of a commercial 7N01 Al-Zn-Mg alloy, using high angle annular dark field scanning transmission electron microscopy. The evolution from C14-Laves phase to quasicrystalline clusters is illustrated, and five-fold symmetry can be found in both real and reciprocal spaces. Our findings reveal the possibility of quasicrystalline formation from Laves phase in a highly plastic metal matrix like Al and demonstrate the structural relationship between Laves phase and quasicrystals.
<b>Suggested Reviewers:</b>	Lipeng Ding, PhD Professor, Nanjing Institute of Technology lipeng.ding@njtech.edu.cn  Calin Daniel Marioara, PhD Senior Research Scientist, SINTEF Industry Calin.D.Marioara@sintef.no  Zhiqing Yang, PhD Professor, Chinese Academy of Sciences yangzq@imr.ac.cn  Gang Ji, PhD Professor, University of Lille gang.ji@univ-lille.fr
<b>Response to Reviewers:</b>	

**Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

## Cover letter

Dear Editor of *Materials Characterization*,

We would like to submit the enclosed manuscript entitled “**Quasicrystalline clusters in C14-MgZn<sub>2</sub> nanoprecipitates in Al alloys**” by Tong Yang, Kai Li, Dominique Schryvers *et al.* to *Materials Characterization*. This manuscript has neither been accepted/published elsewhere nor rejected by your journal previously.

We believe that this manuscript will be of particular interest to the readers of your journal. Laves phase and quasicrystals are both widely investigated, and they have some common characteristics in structures, but the phase transformation between them was seldom reported especially in a highly plastic metal matrix like Al. It is generally acknowledged the precipitation sequence in Al-Zn-Mg-based alloys is: SSSS → GP zone →  $\eta'$ (Mg<sub>2</sub>Zn<sub>3</sub>Al<sub>4</sub>) →  $\eta$ (MgZn<sub>2</sub>). Therefore, the precipitates in overaged states should be C14-MgZn<sub>2</sub> with TCP structure. However, in our work, we firstly report some ultrafine faulty MgZn<sub>2</sub>-Laves phase precipitates containing quasicrystalline clusters in traditional commercial Al alloys, which are much deviated from its standard C14-Laves structure. The Fast Fourier Transform (FFT) patterns of precipitates shows characteristics of five-fold symmetry, corresponding to the simulated FFT pattern of the famous 3D Penrose tiling for quasicrystal. The structural evolution from standard C14-Laves phase to quasicrystalline clusters is demonstrated, and the relationship between C14-Laves phase and five-fold symmetry quasicrystals are also illustrated, providing novel perspectives to understand the definition boundary between quasicrystals and traditional crystals.

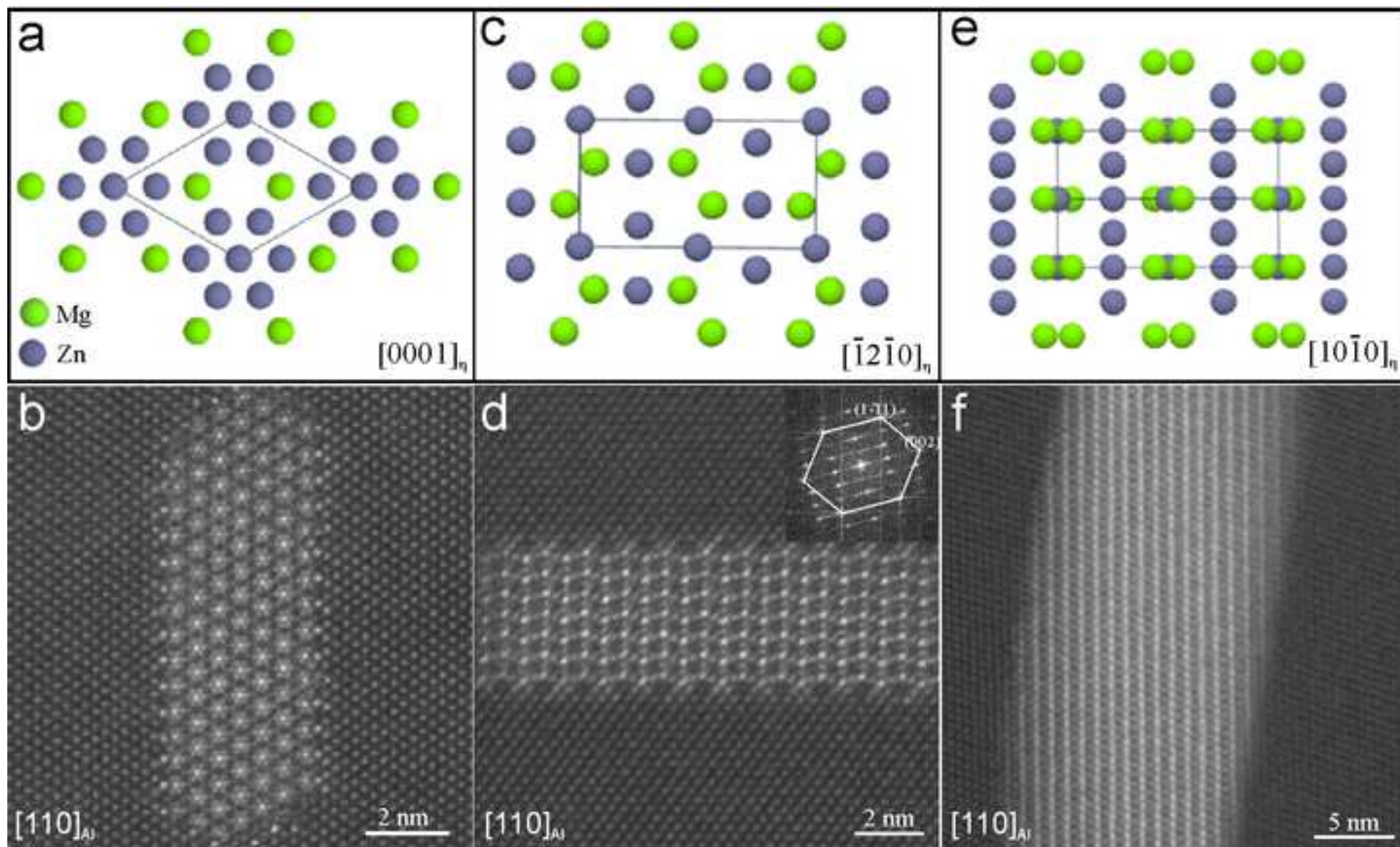
We deeply appreciate your consideration of our manuscript, and we look forward to receiving comments from you and the reviewers.

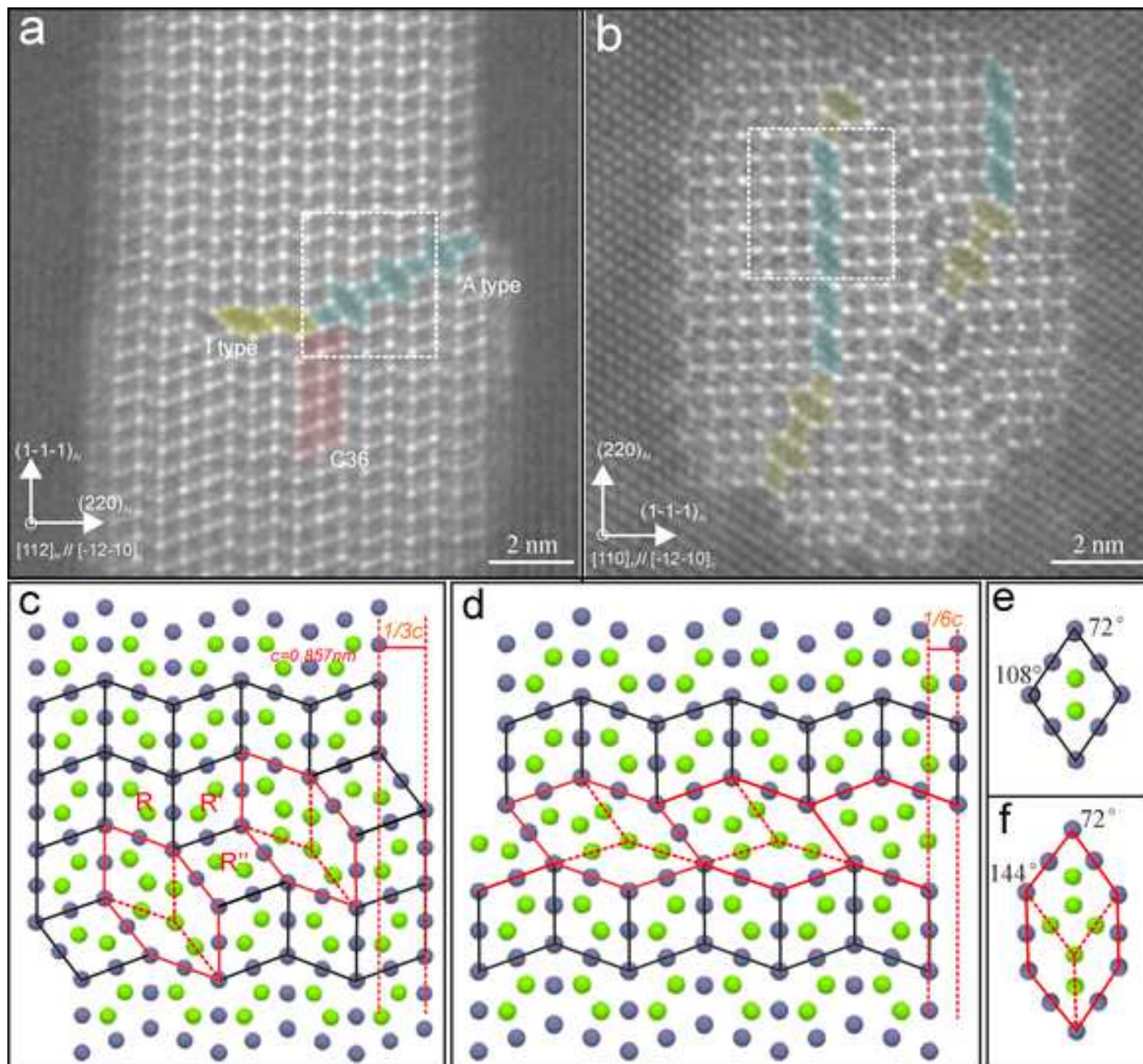
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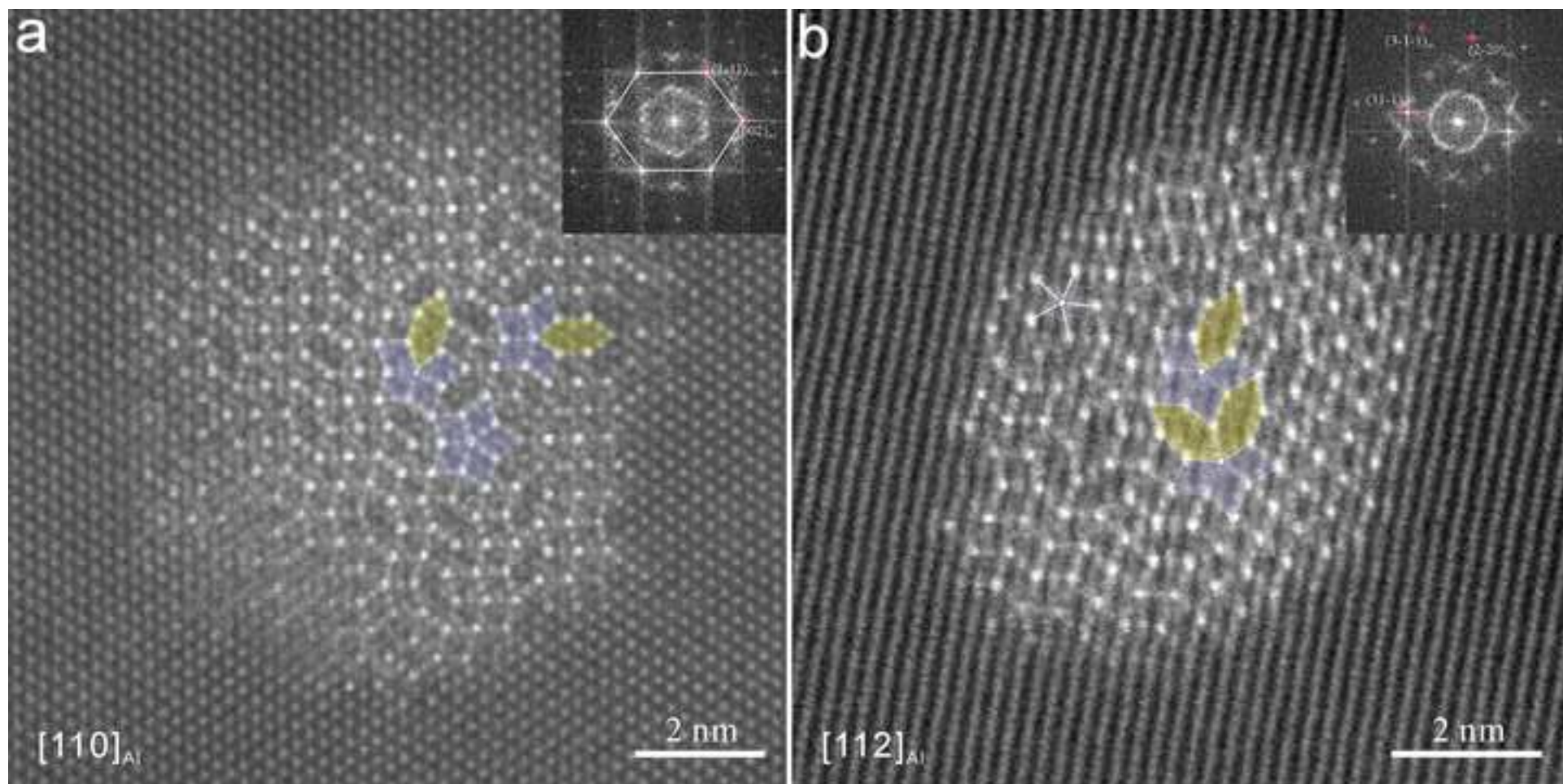
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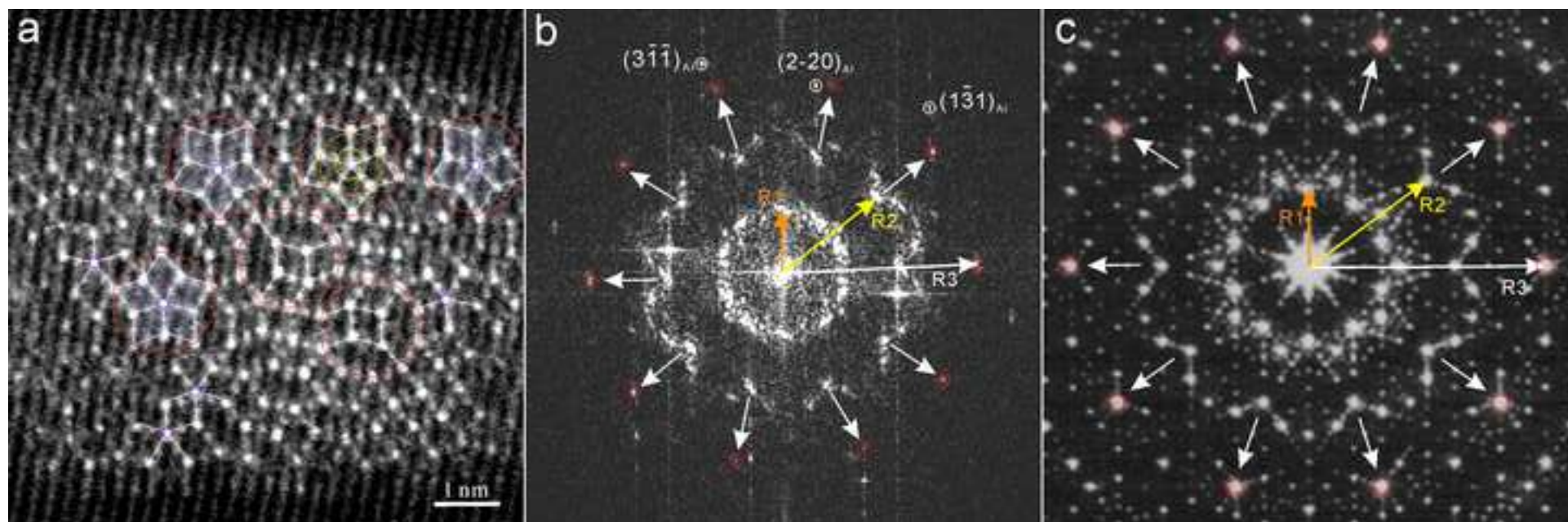
Tong Yang, Yi Kong, Kai Li\*, Qiang Lu, Yucheng Wang, Yong Du, Dominique Schryvers

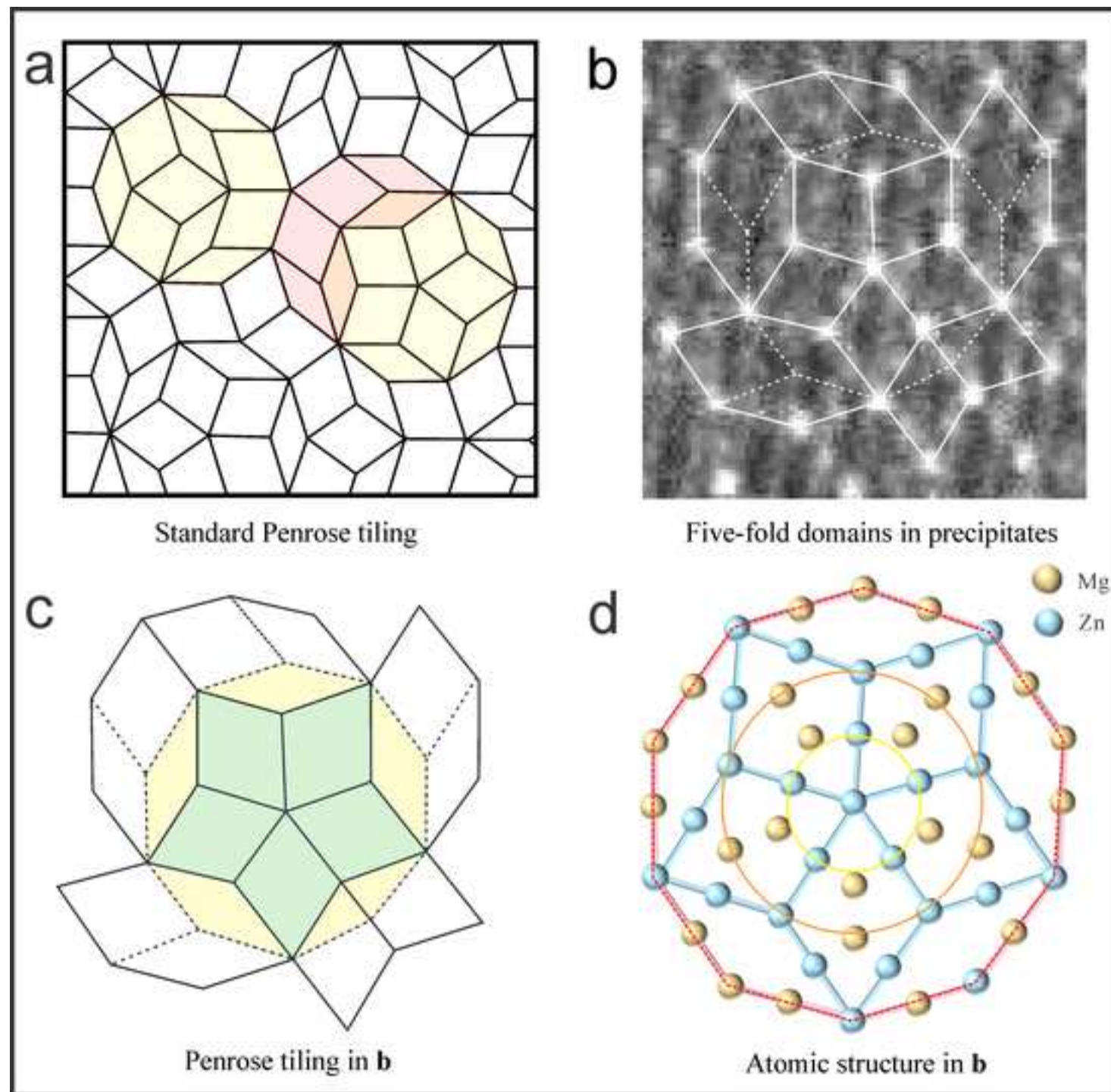
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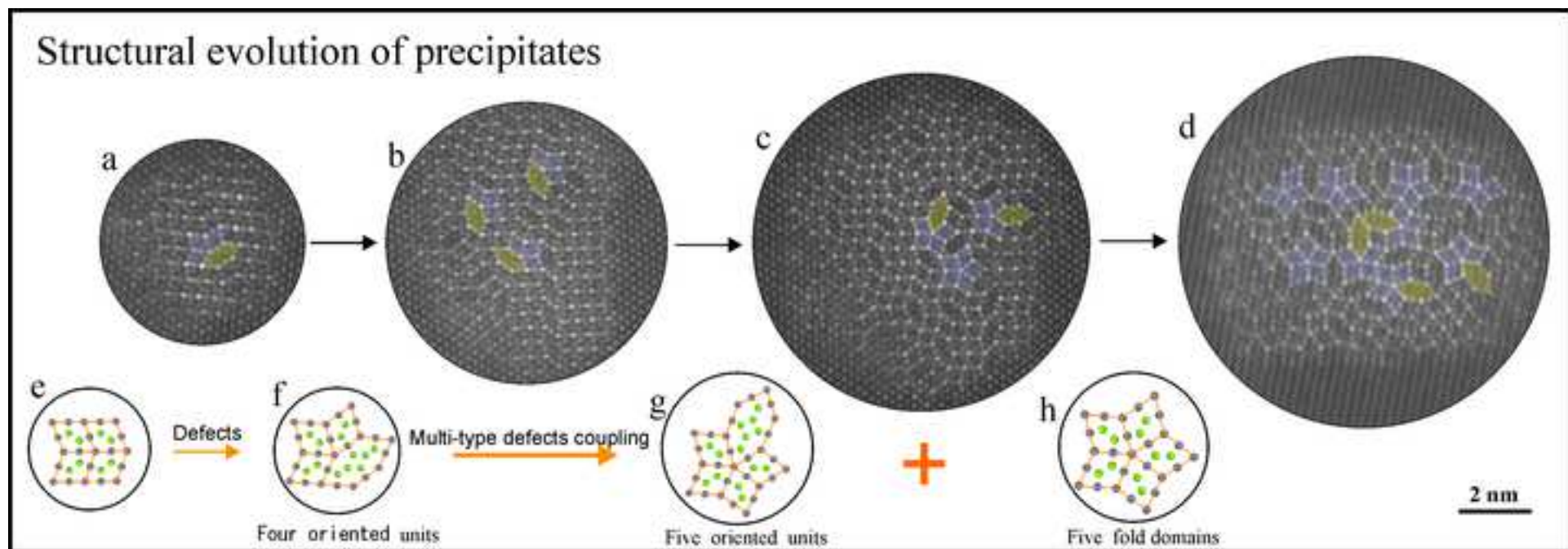












## Highlights

1. Ultrafine faulty  $\text{MgZn}_2$ -Laves phase precipitates containing quasicrystalline clusters in traditional commercial Al alloys were firstly reported.
2. The structural evolution from standard C14-Laves phase to quasicrystalline clusters is demonstrated.
3. The relationships between C14-Laves phase and quasicrystals are illustrated, providing novel perspectives to understand the boundary between quasicrystals and traditional crystals.

# 1 **Quasicrystalline clusters transformed from C14-MgZn<sub>2</sub> nanoprecipitates in** 2 **Al alloys**

3 **Tong Yang<sup>a,b</sup>, Yi Kong<sup>a</sup>, Kai Li<sup>a,c,\*</sup>, Qiang Lu<sup>a</sup>, Yucheng Wang<sup>a</sup>, Yong Du<sup>a</sup>, Dominique Schryvers<sup>b</sup>**

4 <sup>a</sup>State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, China

5 <sup>b</sup>Electron Microscopy for Materials Science (EMAT), University of Antwerp, Antwerp B-2020, Belgium

6 <sup>c</sup>Hunan Center for Electron Microscopy, Central South University, Changsha 410083, China

## 7 **Abstract**

8 Ultrafine faulty C14-MgZn<sub>2</sub> Laves phase precipitates containing quasicrystalline clusters and  
9 demonstrating the formation of binary quasicrystalline precipitates with Penrose-like random-tiling  
10 were observed in the over-aged FCC matrix of a commercial 7N01 Al-Zn-Mg alloy, using high angle  
11 annular dark field scanning transmission electron microscopy. The evolution from C14-Laves phase  
12 to quasicrystalline clusters is illustrated, and five-fold symmetry can be found in both real and  
13 reciprocal spaces. Our findings reveal the possibility of quasicrystalline formation from Laves phase  
14 in a highly plastic metal matrix like Al and demonstrate the structural relationship between Laves  
15 phase and quasicrystals.

16 **Keywords:** Lave phase; Quasicrystals; HAADF-STEM, Five-fold symmetry.

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18 **\*Corresponding author:**

19 Kai Li: [leking@csu.edu.cn](mailto:leking@csu.edu.cn) ( [ORCID number : 0000-0002-9645-4896](#) )

## 1 **1. Introduction**

2 Laves phases and quasicrystals have some common characteristics in structures,  
3 possessing a rather high and uniform packing density of atoms [1], defined as well-known  
4 tetrahedrally close packed (TCP) structures. The classification of TCP structures includes the  
5 well-known Frank–Kasper and Friauf–Laves structures, with limited coordination numbers of  
6 12, 14, 15 and 16 [2]. In the meantime, quasicrystals are also grouped into ‘Frank–Kasper’  
7 class according to their chemistry and local order [3]. Two kinds of quasicrystals are widely  
8 investigated: 3D icosahedral quasicrystals [4,5] and 2D decagonal quasicrystals [6,7]. Friauf–  
9 Laves structures constitute a huge class of intermetallic compounds which can be formed  
10 from element combinations all over the periodic table resulting in a huge number of known  
11 examples. Fritz Laves divided these compounds into 3 types, including the cubic C15-  
12 MgCu<sub>2</sub> type, the hexagonal C14-MgZn<sub>2</sub> and C36-MgNi<sub>2</sub> types [8-11]. In Al-Zn-Mg alloys,  
13 the precipitation sequence is SSSS → GP zone → η' (Mg<sub>2</sub>Zn<sub>3</sub>Al<sub>4</sub>) → η (MgZn<sub>2</sub>) [12-16],  
14 while the precipitates in overaged Al-Zn-Mg alloys are mainly C14-MgZn<sub>2</sub> with TCP  
15 structure.

16 The structural connections between quasicrystals and TCP structures, especially Laves  
17 structures, has been intensively studied in metallic systems. As we found in Al-Zn-Mg alloys  
18 before, stacking faults or planar defects can separate the C14-MgZn<sub>2</sub> Laves phase into several  
19 domains, resulting in complicated structures including a five-fold symmetry cluster in MgZn<sub>2</sub>  
20 precipitates [17]. However, it is not known what such a single cluster implies. Many five-fold  
21 symmetry structures of these Laves phase particles were also found in some other systems  
22 especially in Mg alloys. According to the investigation of Ye et al. [18,19] on Fe-based  
23 superalloys, differently oriented domains of TCP phases (C14, C15 and others) intergrow  
24 frequently with a fairly good match at the interphase boundaries. Most importantly, they  
25 found that all electron diffraction patterns of these phases contained a five-fold symmetry

1 distribution of 10 diffraction spots at the same circle. They reported that this five-fold  
2 symmetry came from two pentagonal prisms superposed in anti-symmetrical positions, i.e.,  
3 one prism rotated around its 5-fold symmetry axis with respect to the other by 180°. The  
4 faultier the structure, the more obvious the five-fold symmetry of the diffraction pattern.  
5 Recently, Yang et al. [20] found that in Mg-Zn alloys, the formation of extended binary  
6 quasicrystalline precipitates with Penrose-like random-tiling structures began with chemical  
7 ordering within the pentagonal structure at cores of prismatic dislocations. They stated that  
8 their binary quasicrystalline phase was formed by dislocation-assisted precipitation, and the  
9 initial icosahedral cluster also originated from TCP structures including C14 Laves and  $\mu$   
10 phases. Moreover, their quasicrystalline precipitates were formed by random tiling of these  
11 rhombic and hexagonal tiles, showing good five-fold symmetry with 10 spots in Fast Fourier  
12 transform (FFT) patterns. Bendo et al. [21] concluded that in deformed Mg-Zn alloys,  
13 precipitates nucleating on dislocations can grow into quasicrystalline structures made of  
14 rhombic and hexagonal tiles, in contrast to C14-MgZn<sub>2</sub> Laves crystals precipitating inside  
15 undeformed Mg matrixes.

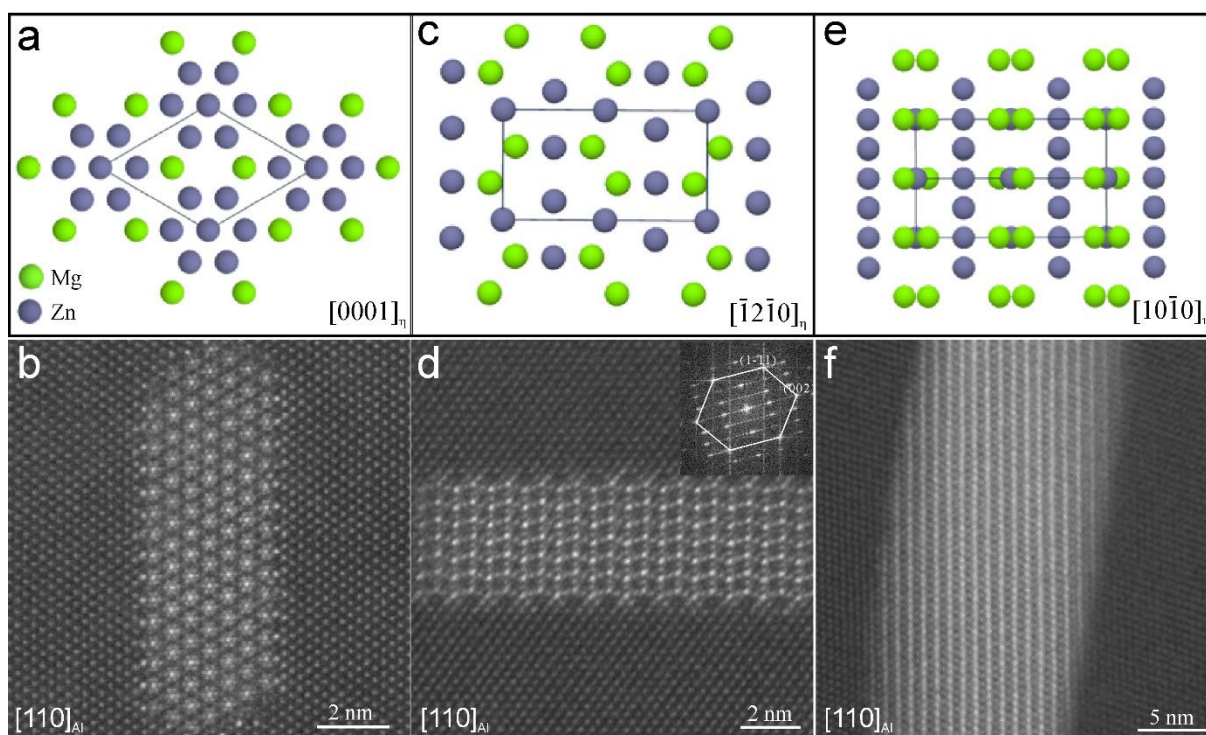
16 However, in the Al-Zn-Mg-based alloy system, the C14-MgZn<sub>2</sub> Laves phase was  
17 frequently reported as the main precipitate in the over-aged state and no quasicrystalline  
18 nano-precipitates was reported yet, although our recent finding of a submicron core-shell  
19 quasicrystalline particle in an Al-Zn-Mg alloy with Fe and Ni impurities revealed the  
20 possibility of formation of quasicrystals in traditionally processed Al alloys [22]. Here we  
21 clarified the evolution from Laves phase to quasicrystalline clusters in MgZn<sub>2</sub> precipitates,  
22 taking the structural transformation of C14-MgZn<sub>2</sub> Laves phase precipitates in Al-Zn-Mg  
23 alloy as an example. Our findings provide some unique perspectives for the boundaries  
24 between traditional crystal structures and quasicrystals.

25

## 1 **2. Methods**

2 A commercial 7N01 Al-Zn-Mg alloy with 4.31% Zn, 1.41% Mg, 0.31% Mn, 0.14% Fe  
3 and 0.12% Cu (in wt.%) aged at 120° for 568 h (T5 state) was used. More details for the alloy  
4 fabrication and TEM sample preparation can be found in our previous work on the same alloy  
5 [17]. Samples for TEM were mechanically polished to a thickness of 50-100 μm, and then  
6 punched into disks with a diameter of 3 mm. The disks were electropolished in a Struers  
7 TenuPol-5 twin-jet instrument using a solution of 70 vol.% methanol and 30 vol.% nitric acid  
8 at a polishing temperature of −30 °C. The voltage of electropolishing was 14 V and the  
9 current stabilized at 0.2 A. A FEI Titan G2 60-300 TEM with a probe (spherical aberration)  
10 corrector operating at 300 kV was used to observe the samples at micro to atomic scales  
11 using high angle annular dark field scanning transmission electron microscopy (HAADF-  
12 STEM). The beam convergence semi-angle of the Titan microscope was 21 mrad. The  
13 HAADF detector collects electrons that pass close to the atomic nuclei, and thus scatter with  
14 intensities that approach the  $Z^2$  dependency of Rutherford scattering. Therefore, local  
15 structural and chemical information can be obtained with atomic resolution by HAADF-  
16 STEM imaging.

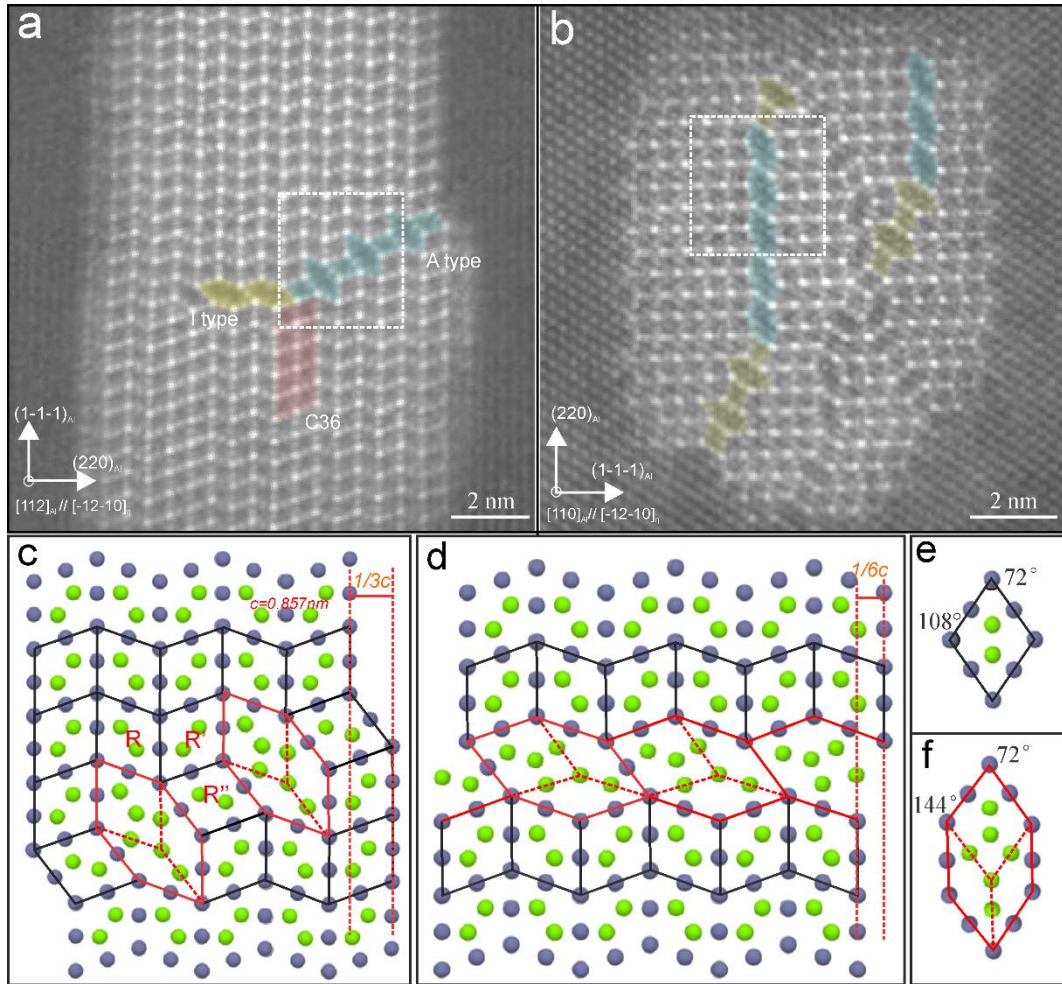
## 17 **3. Results**



**Figure 1** Model of perfect C14 Laves phase structure and corresponding atomic-scale images in the current alloy. **a**, **c** and **e** display the model of  $\text{MgZn}_2$  [10] viewed from  $[0001]_\eta$ ,  $[\bar{1}2\bar{1}0]_\eta$ ,  $[10\bar{1}0]_\eta$  directions, respectively. **b**, **d** and **f** display atomic scale HAADF-STEM images taken from  $[110]_{\text{Al}}$ .

$\eta$ - $\text{MgZn}_2$  phase, the prototype of the C14 Laves phase, was found as the majority of the nano-precipitates in the current alloy. The space group of  $\text{MgZn}_2$  is  $P6_3/mmc$ , and the lattice parameters are  $a = b = 0.522 \text{ nm}$ ,  $c = 0.857 \text{ nm}$ ,  $\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$  [10]. Figure 1 shows the model of perfect C14 Laves structure and corresponding atomic-scale images by HAADF-STEM along different zone axes. In these HAADF-STEM images, the heavier Zn atoms show a much higher intensity than the lighter Mg atoms ( $Z_{\text{Zn}} = 30$ ,  $Z_{\text{Mg}} = 12$ ), the strongest intensities further corresponding to the atom columns containing the most densely arranged Zn atoms (see the Supplementary image in Fig. S1 for a 3D view). Individual Zn atomic columns as seen in the  $[0001]_\eta$  axis, i.e., the top view of the HCP structure, are well distinguished in atomic resolution HAADF-STEM images. These particles display a plate-

1 like shape under  $[0001]_{\eta}$  as shown in Fig. 1b. The orientation of this particle in the Al matrix  
 2 in Fig. 1b is as follows:  $[0001]_{\eta} // [110]_{Al}$ ,  $(10-10)_{\eta} // (002)_{Al}$ . As for the other side view of  
 3 such a particle in Fig. 1d, the Zn atomic arrangement in  $MgZn_2$  precipitates shows a zig-zag  
 4 structure, which is again perfectly corresponding with the crystal mode of C14 Laves phase.  
 5 Moreover, the orientation of this particle with the Al matrix in Fig. 1d can be determined as  
 6 follows:  $[-12-10]_{\eta} // [110]_{Al}$ ,  $(10-10)_{\eta} // (002)_{Al}$ . These two particles thus both belong to the  
 7  $\eta_1$  orientation of  $(10-10)_{\eta} // (001)_{Al}$ ,  $[-12-10]_{\eta} // [110]_{Al}$ ,  $[0001]_{\eta} // [110]_{Al}$ . The precipitate  
 8 shown in Fig. 1f belongs to the  $\eta_2$  orientation, which is  $(0001)_{\eta} // (1-1-1)_{Al}$ ,  $[10-10]_{\eta} // [110]_{Al}$   
 9 [12].



11 **Figure 2** Different types of hexagonal units in Laves phase. **a-b** HAADF-STEM images of  
 12  $MgZn_2$  precipitates with defects containing hexagonal units. **c-d** Schematic diagrams of the



1 atomic structures in the white frames in **a-b**. **e-f** Schematic diagram of the structures for  
2 rhombic and hexagonal units, respectively. Zone axis is  $[112]_{Al}$  in **a** and  $[110]_{Al}$  in **b**, both are  
3 parallel to  $[-12-10]_{\eta}$ .

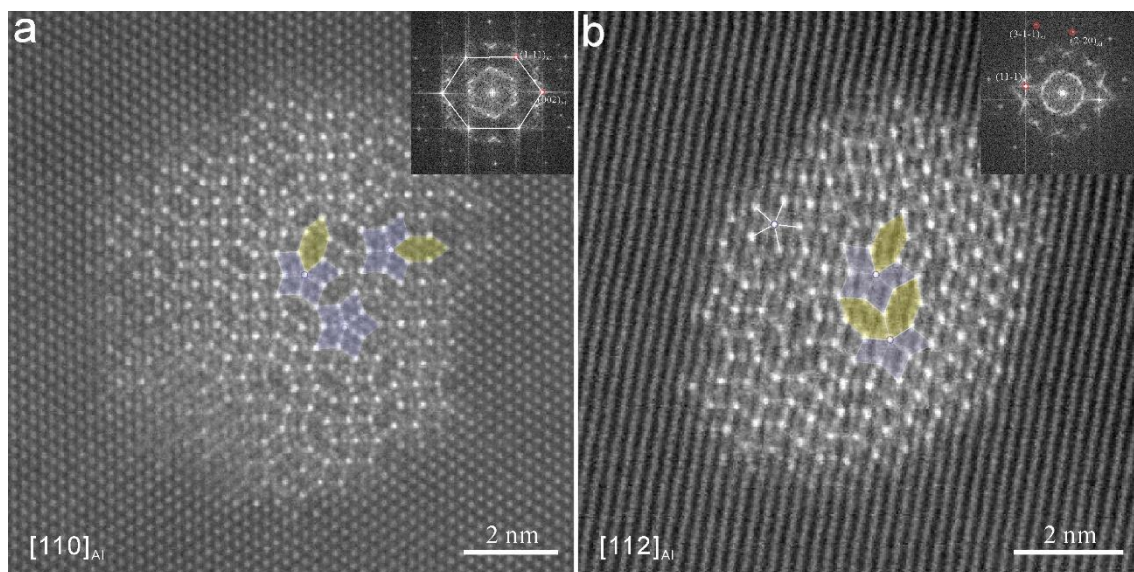
4 However, except for those perfect C14 Laves phase precipitates, there are a large  
5 number of  $MgZn_2$  precipitates with various defects inside, as displayed in Fig. 2a-2b. These  
6 defect structures are assumed to occur by the interaction between dislocations and  
7 precipitates or due to the strain between the matrix and the precipitates [23]. The regular Zn  
8 atom arrangements in the  $MgZn_2$  phase are like zig-zag structures with rhombuses,  
9 possessing R sub-units (the rhombic sub-unit) and R' sub-units (the  $180^\circ$ -rotated rhombic sub-  
10 unit). However, for those precipitates with defects, the perfect zig-zag structure is interrupted  
11 by a type of hexagonal unit. Due to the atomic plane slip, the upper and bottom parts of  
12 perfect C14 structure cannot connect smoothly, as indicated in Figs. 2c-2d. The appearance of  
13 these special planar defects with hexagonal structures is inferred as self-accommodating  
14 defects, which can accommodate the lattice mismatch between the matrix and the precipitates  
15 and thus relieve the strain inside these precipitates [17]. The hexagonal structures can mainly  
16 be divided into two groups according to the different slip distances: in one group the  
17 hexagonal units alternate with rotated R units (named as R''), as indicated by blue background  
18 in Fig. 2a, while in the other group the hexagonal units are interconnected as shown with  
19 yellow background in Fig. 2a and also in Fig. 2b. These bands of planar defects are defined as  
20 A type and I type, respectively. Different mechanisms for the formation of these two kinds of  
21 hexagonal structures are demonstrated in Figs. 2c-2d. If the atomic plane displacement is  $1/3$   
22  $c$  ( $c = 0.857$  nm for  $\eta$ - $MgZn_2$ ) as denoted in Fig. 2c, the A type band occurs. In contrast, if the  
23 atomic plane displacement is  $1/6 c$  as denoted in Fig. 2d, the I type band is formed.  
24 Meanwhile, these two ways (A type and I type) can be combined in one precipitate to form  
25 faultier structures. For example, in Fig. 2a, the A type can twist to I type due to the existence

1 of stacking faults (C14-C36, see red background in Fig. 2a). Similarly, in Fig. 2b, several  
2 bands of *A* type together with *I* type structures were also found. These hexagonal units were  
3 frequently observed in C14 Laves precipitates in the current Al-Zn-Mg alloy.

4 As for the hexagonal tiling units, in Mg-Zn-based system, it was reported that these  
5 structures are from monoclinic  $Mg_4Zn_7$  phase containing periodically arranged rhombic and  
6 hexagonal units, which is analogous to Laves phases and has been detailed characterized by  
7 Singh and Rosalie et al. [24-26]. However, no single  $Mg_4Zn_7$  phase is reported yet in the  
8 precipitation sequence of Al-Zn-Mg-based alloys. Regarding the existence of hexagonal tiles  
9 of C14-Laves phase in Al-Zn-Mg alloys, Chung et al. [12] also compared it with  $Mg_4Zn_7$  in  
10 7050 aluminium alloys. In their opinions, they concluded the continuously connected  
11 flattened hexagonal units are completely inconsistent with the typical structure of  $Mg_4Zn_7$ ,  
12 and they regarded the stacking faults formed from hexagonal units as antiphase boundary.

13 Here in our observation, the appearance of hexagonal tiling units cannot be simply  
14 regarded as part of  $Mg_4Zn_7$  phase. The  $Mg_4Zn_7$  phase is still a periodic crystalline structure  
15 with a monoclinic unit cell but these hexagonal tiles in our precipitates are shown as  
16 nonperiodic, corresponding more to the random formation of defects. Besides, it is hard to  
17 find one  $Mg_4Zn_7$  monoclinic unit in these observed precipitates. And the band of stacking  
18 faults by hexagonal units can even be bent with different orientations (as shown in Fig. 2b),  
19 which cannot be defined as the structure of  $Mg_4Zn_7$  phase.

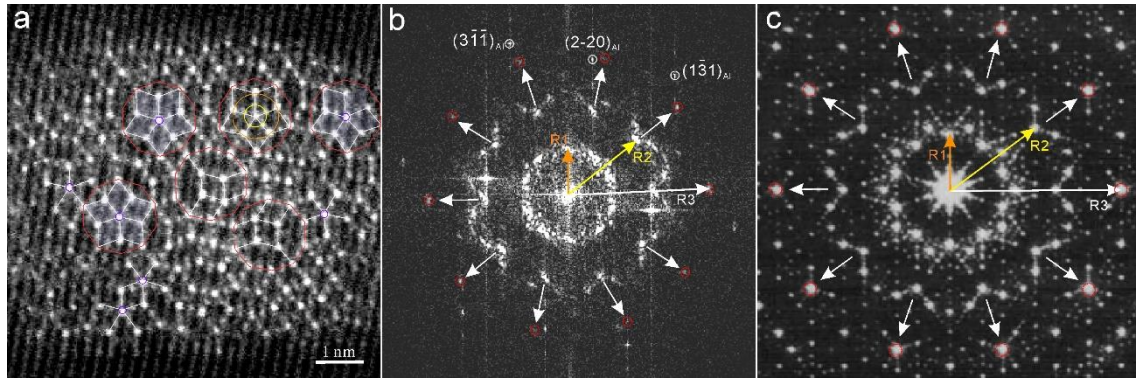
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1

2 **Figure 3** HAADF-STEM image of two particles with a high-density of defects. Matrix zone  
 3 axis is  $[110]_{Al}$  in **a** and  $[112]_{Al}$  in **b**, both are parallel to  $[-12-10]_{\eta}$ . FFT patterns of these  
 4 particles are added as insets.

5 With the increase of the number of such defect structures, the zig-zag atomic  
 6 arrangement of a perfect C14 Laves phase will greatly change, and even the morphology will  
 7 change accordingly to be more equiaxed, as shown in Fig. 3. This is consistent with our  
 8 previous findings in another paper [17]. It can be seen that in these atomic scale images, there  
 9 are also a large number of hexagonal units in these precipitates. Compared with Fig. 2, these  
 10 structural units are arranged without rules, similar to Penrose-like random tiling, making  
 11 these particles greatly deviating from the standard C14 structure. Many five-fold cross-points  
 12 are indicated in Figs. 3a-3b, and the correspondingly inserted FFT patterns resemble those  
 13 from quasicrystals instead of Laves phase.



1

2 **Figure 4** Quasicrystalline clusters in Laves phase. **a** HAADF-STEM image of particles with  
 3 many five-fold cross-points. Zone axes are  $[112]_{Al} // [-12-10]_{\eta}$ . **b** FFT pattern from **a**. **c**  
 4 Simulated FFT pattern of the 3D Penrose tiling model for quasicrystals [27].

5 Here we found a typical complex precipitate containing a very high density of defects  
 6 inside, as shown in Figure 4a. It is obvious that the FFT pattern displayed in Fig. 4b is totally  
 7 different from that of perfect C14 Laves phase reported previously. There are 10 outmost  
 8 spots marked by red circles in the FFT pattern, similar to those found by Ye et al. [18] in an  
 9 Fe-based alloy with TCP structure. Besides, other spots in the FFT pattern also display a 10-  
 10 fold symmetry. It should be noted that the FFT pattern in Fig. 3b highly resembles the  
 11 simulated FFT pattern of the famous 3D Penrose tiling for quasicrystal [27] shown in Fig. 4c.

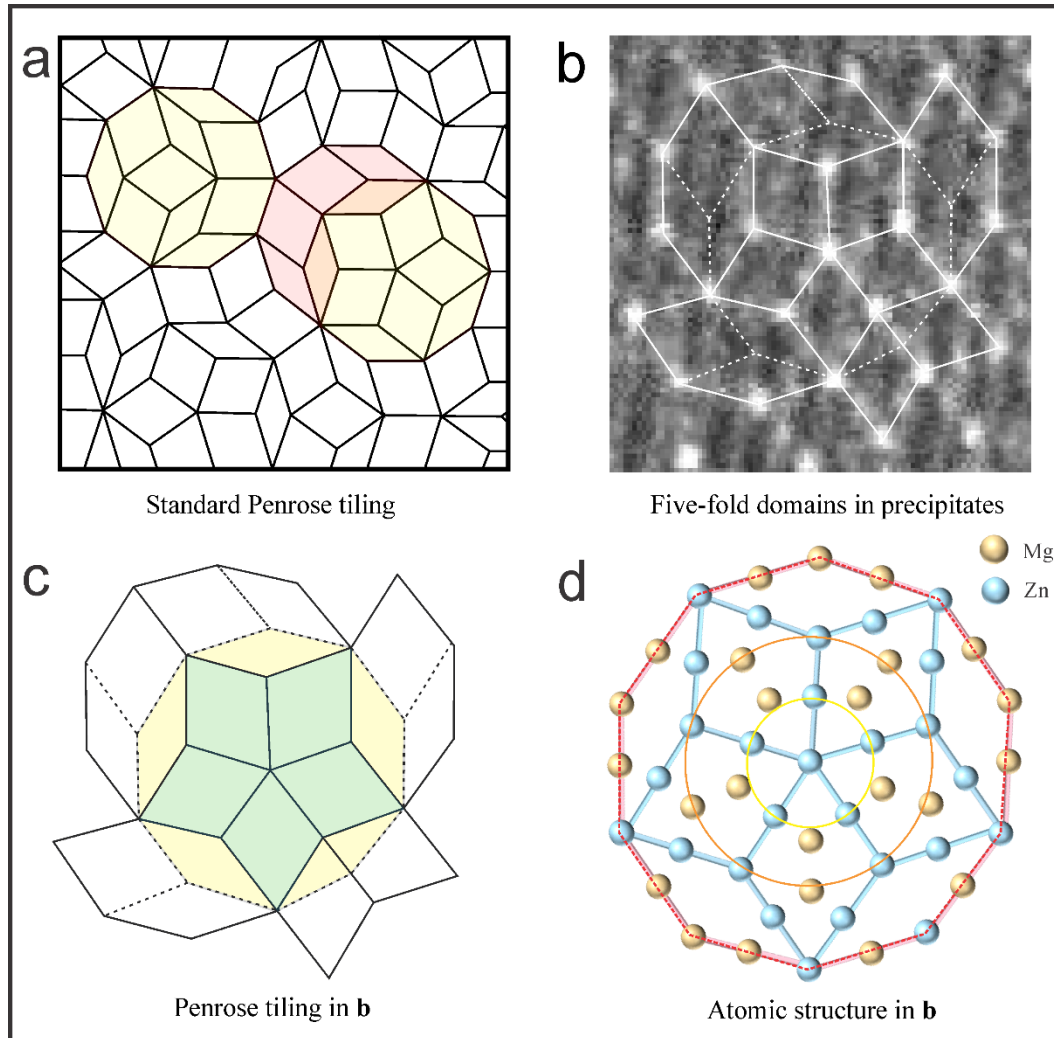
12 The outmost 10 spots in Fig. 4b were also found by Ye et al. [18] in common TCP  
 13 phases in superalloys such as  $\mu$  phase, C14 Laves phase and C phase. Although these  
 14 structures have different lattice parameters and diffraction patterns, they all show a 10-fold  
 15 distribution with 10 strong spots pairs occurring at about  $8 \text{ nm}^{-1}$ . Similarly, the radius of the  
 16 R3 is measured as  $7.20 \text{ nm}^{-1}$  for the current 10-fold symmetry structure, which is close to the  
 17 reciprocal distance for FFT spot  $(2-20)_{Al}$  as shown in Fig. 3b. However, the other two  
 18 diffraction rings marked as R1 and R2 were not observed by Ye et al. [18] in their TCP  
 19 structures. It is also found that there are several five-fold symmetry atomic structures in real  
 20 space shown as a pentagram unit in this particle as displayed in Fig. 4a. Thus, the radii of

1 rings R1 and R2 measured in reciprocal space correspond to the distance between atoms,  
2 marked as orange and yellow circles in real space in Fig. 4a. The relationship between real  
3 and reciprocal space is indicated with the same colour. For example, as can be seen in real  
4 space, the diameter of the orange circle in Fig. 4a is measured as 0.22 nm, corresponding to  
5 the orange line marked as R1 in FFT, which is measured as  $4.50 \text{ nm}^{-1}$  in radius. The distance  
6 of the yellow circle in Fig. 4a is measured as 0.44 nm, corresponding to the yellow line R2 in  
7 FFT in Fig. 4b, which is measured as  $2.25 \text{ nm}^{-1}$  in radius. Outmost ten spots in the  
8 experimental FFT of Fig. 4b (e.g., those noted R3) also match the well-known simulated FFT  
9 of the Penrose tiling in Fig. 4c. In Fig. 4a, there are about 7 cross-points for the five-fold  
10 domains, indicated by purple spots, and they are also marked in Fig. 3. In comparison, the  
11 particle shown in Fig. 3a also contains many hexagonal structures but just one perfect five-  
12 fold domain (see the overlaid lines). The FFT patterns of Figs. 4a, 3a and 3b are all also  
13 similar to the simulated FFT pattern of 3D stack quasicrystals by Mackay [27]. The size of  
14 these precipitates is only 3-5 nm, much smaller than those perfect C14 Laves phase  
15 precipitates. Meanwhile the morphologies are oval-like or round instead of lath-like. These  
16 particles can thus be classified as quasicrystalline clusters with only hexagonal units and  
17 rhombic units, which can infinitely tile the plane randomly and display 10-fold symmetry in  
18 the reciprocal space.

19 In our work, these precipitates are likely to be designated as quasicrystalline clusters  
20 instead of standard quasicrystals or quasicrystal approximants. In previous investigations, the  
21 definition of quasicrystals or quasicrystal approximants are strict [28, 29]. As for quasicrystal  
22 approximants, the substructures or the structural tiles are the same as those of the  
23 corresponding quasicrystals but are arranged periodically in approximants. In other words,  
24 they still possess the characteristics of periodic crystals. Consequently, “quasicrystalline

1 cluster” is more accurate to define such tiny precipitates, and the quasicrystalline  
2 characteristics are discussed in detail below.

### 3 4. Discussion



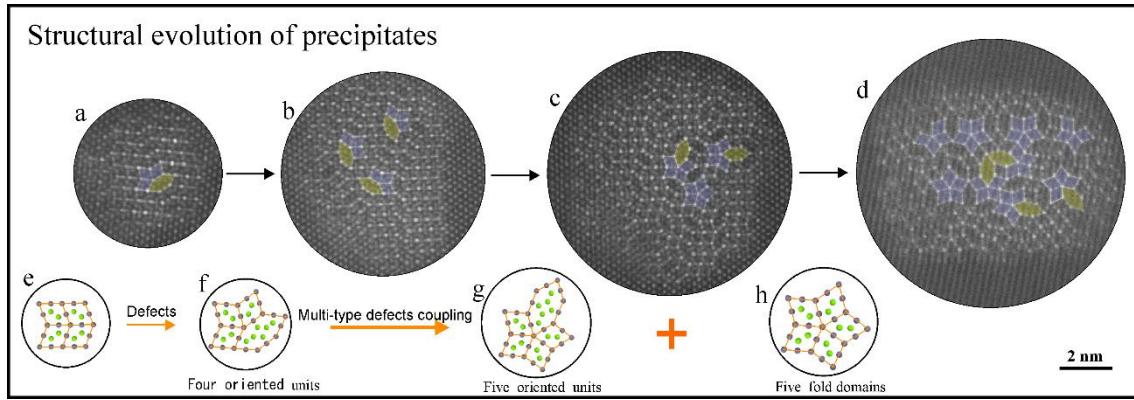
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5 **Figure 5** Schematic diagram of Penrose tiling in precipitates. **a** Standard Penrose tiling model,  
6 typically used for understanding the two-dimensional quasiperiodic structures in quasicrystals.  
7 **b** Part of precipitates including five-fold domains. **c** Penrose tiling in **b**. **d** Atomic structure  
8 demonstration in **b** with five-fold symmetry.

#### 9 4.1 Penrose tiling in Laves phases

1 Figure 5 provides a schematic diagram of Penrose tiling in precipitates to demonstrate  
2 the similarity between five-fold structural units in the defective Laves phase precipitate and  
3 Penrose tiling.

4 The two-dimensional Penrose tiling has been regarded as an influential model for  
5 understanding quasicrystals' structure [30, 31], in which two types of tiles are laid down  
6 according to matching rules to form a five-fold symmetric quasiperiodic pattern. Therefore,  
7 part of standard Penrose tiling is used in Fig. 5a to describe the projection characteristics of  
8 quasicrystals [32]. In comparison, part of the atomic structure from Fig. 4a is chosen for  
9 analysis in detail in Fig. 5b, with white lines overlaying the five-domain structure comprised  
10 of hexagonal and rhombic units. Dashed lines are also plotted in hexagonal structures in Figs.  
11 5b and 5c, dividing each of them into 2 slim rhombic units and one broader rhombic unit.  
12 These totally conform to the typical Penrose tiling rules, only with two kinds of rhombic units  
13 to tile the whole plane. The atom column projection along the five-fold axis of the  
14 quasicrystalline cluster in the Laves phase is illustrated in Fig. 5d. It is found that both Zn  
15 arrangements and Mg arrangements can form a well-defined five-fold symmetry. Most  
16 importantly, the red dashed lines in Fig. 5d form a decagonal unit. This confirms that the  
17 observed structures in Figs. 5b and 4a are highly similar to a quasicrystal in atomic  
18 arrangement, accounting for the quasicrystalline characteristics found in the FFT pattern in  
19 Fig. 4b.

## 20 4.2 Structural evolution from Laves phase to five-fold symmetric particles



**Figure 6** Schematic diagram of structural evolution of precipitates.

Figure 6 displays the detailed structural evolution during precipitate coarsening. Four different-sized precipitates from 2 nm to 5 nm are characterized to show the evolution process. As displayed in the first precipitate in Fig. 6a, when it is tiny (1-2 nm), initial defects can appear inside, making the standard Laves structure transform into four oriented units with three rhombic tiles and a hexagonal tile (see Fig. 6f). During precipitate coarsening, multi-type stacking faults or defects can be coupled together. Moreover, due to the special zig-zag structure of Laves phase, the rhombic tiles from Laves phase can easily transverse its growth direction by synchroshear [33], creating more possibilities for formation of five-fold symmetry structures (see Fig. 6c). With the size increased during precipitates growth, complex defects simultaneously couple inside the precipitate, and more and more five-fold symmetry structures appear, when a strong and complicated strain field probably exists around the precipitate according to our previous work [17]. These structural changes make the precipitates grow in an oval-like or round-like morphology, which can also help to decrease the interfacial energy and relieve the internal strain as well.

### 4.3 Different formation mechanism of quasicrystalline particles in Mg and Al alloys

In Mg alloys, such kind of transformations from Frank-Laves structures to quasicrystalline clusters are much more common. As is known, HCP Mg structure has less dislocation slip systems compared with FCC Al, therefore many other plastic deformation



1 methods, like stacking faults, twins, long period stacking ordered (LPSO) structures, are self-  
2 generated to accommodate the structure in the Mg matrix to deformation/stress. Moreover,  
3 according to the molecular dynamics simulation by Yang et al. [20] about prismatic edge <a>  
4 dislocation cores in Mg matrix at different temperatures of 0 K, 300 K and 600 K, the five-  
5 fold atomic clusters can be formed from dislocation cores and they were found to remain  
6 stable when the temperature is increased to 600 K.

7 However, the formation mechanism of quasicrystalline clusters in Al alloys is different.  
8 All the plastic deformation methods mentioned above, except for dislocation slip, are difficult  
9 in traditional Al alloys. The stacking fault energy in Al (160-250  $\text{mJ}\cdot\text{m}^{-2}$  [34, 35]) is much  
10 higher than that in Mg (125  $\text{mJ}\cdot\text{m}^{-2}$  [36]). It is inferred that, when strain exists in an Al alloy,  
11 precipitates tend to adjust their internal structure and accommodate to the strain, e.g., by  
12 generating defect bands comprised of hexagonal and rhombic units in C14-MgZn<sub>2</sub>  
13 precipitates as illustrated in detail in Fig. 2, which is another way to resist plastic deformation  
14 in Al-based alloys. Another example is that the semi-coherent  $\beta''$ -Al<sub>2</sub>Mg<sub>5</sub>Si<sub>4</sub> nanoprecipitates  
15 [37] and other nanoprecipitates like B' in Al-Mg-Si alloys [38], were observed to generate  
16 internal stacking faults during coarsening, to accommodate themselves to the strain caused by  
17 lattice misfit. Meanwhile, in our previous investigation by Geometric Phase Analysis (GPA)  
18 [17], it was also proved that these self-assembled structures are mainly driven by strain  
19 around the precipitates due to lattice misfit. This self-assembling mechanism is supposed to  
20 be different from the dislocation core mechanism found in Mg alloys.

## 21 **5. Conclusions**

22 In our work by HAADF-STEM observations, we found some ultrafine faulty MgZn<sub>2</sub>  
23 Laves phase precipitates containing quasicrystalline clusters, strongly deviating from the  
24 expected C14-Laves structure. The corresponding FFT pattern shows characteristics of five-

1 fold symmetry, similar to the simulated FFT pattern of the 3D Penrose tiling for quasicrystal.  
2 Our conclusions further explain the formation mechanism of 5-fold symmetry diffraction  
3 patterns of Laves phases. The structural transformation from standard C14-Laves phase to  
4 quasicrystalline clusters comprised of rhombic and hexagonal units is demonstrated, and the  
5 relationship between C14-Laves phase and five-fold symmetry quasicrystals is also illustrated  
6 in detail, providing novel perspectives to understand the definition boundary between  
7 quasicrystals and traditional crystals.

8

## 9 **Contributions**

10 **Tong Yang:** Conceptualization, investigation, writing Original Draft, writing  
11 reviewing, and editing. **Kai Li:** Supervision, funding acquisition, writing reviewing, and  
12 editing. **Dominique Schryvers:** Supervision, writing reviewing, and editing. **Yong Du:**  
13 Project administration, Funding acquisition. **Yi Kong, Qiang Lu and Yucheng Wang:**  
14 Discussion and editing.

15

## 16 **Declaration of competing interests**

17 The authors declare that they have no known competing financial interests or personal  
18 relationships that could have appeared to influence the work reported in this paper.

## 19 **Acknowledgments**

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21 China (51820105001 and 52071340) and China Scholarship Council for Tong Yang's Joint-  
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23 Lars Riekehr at EMAT of the University of Antwerp for the assistance in training and use of

1 the TEM and of Saeid Pourbabak for the sample preparation. Elsevier is acknowledged for  
2 providing the permission of reusing Figure 4c.

### 3 **Data Availability**

4 Data will be made available on request.

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7 interfaces of the B' precipitate in Al-Mg-Si alloys, *Acta Mater.*, 185 (2020) 193-203.

8

**Dear Editor and Reviewers,**

All the authors would like to thank you for the time and effort spent in reviewing the manuscript. We greatly appreciate your valuable comments. All these comments are carefully considered and responded accordingly in the following section. Revisions in the manuscript are marked in red.

We sincerely hope you can be satisfied with these revisions.

All the best,

Kai Li, on behalf of all authors

Review comments:

**Reviewer #1:** This work extends the report of Yang, L. Zhang, M.F. Chisholm, et al., Precipitation of binary quasicrystals along dislocations, Nat. Commun., 9 (2018) 809-815.

(1) The structure shown in Fig. 4a is well appreciated, but comparing the FFT of Fig. 4b to simulated pattern of a Penrose tiling (Fig. 4c) is an overclaim! Instead, authors could try to explain what kind of defect in the matrix can give rise to this structure in the precipitate.

**Response:** Thank you for your comment. As for the comparison between simulated FFT pattern of a Penrose tiling (Fig. 4c) and the FFT pattern of the experimental image shown in Fig. 4b, we admit there are still many differences in detail between these patterns, because the precipitates' size is extremely tiny and Penrose tiling is defined as an infinite tile in the whole plane. Here we would like to illustrate that the principles are consistent by this kind of comparison except for the size. The precipitate structure shown in Fig. 4a is also formed by two kinds of units (or tiles), randomly tiled in the projected plane in a way similar to quasicrystals, and then forming a FFT pattern similar to that in Fig. 4c. According to your comment, we would like to term the structure as an immature quasicrystal which contains quasicrystalline clusters and loses crystalline features.

As for the formation reason of this structure, now we can hardly tell an accurate trigger in our alloys. However, in literatures, almost all the reported QC or QC approximants related to Laves phases are in Mg-based systems. According to Yang et al.'s experimental results and molecular calculations [Z. Yang, M.F. Chisholm, et al., Nat. Commun., 9 (2018) 809-815], they concluded these QCs precipitated along dislocations. However, for Al-based systems, we haven't found similar reports but here we still believe it should be related to severe deformation or high strain surrounding precipitates. And we also discussed about it in **4.3 Discussion part, Page 15, Line 8**, marked in red. These scientific problems about the trigger are also our work prospects in the future to verify our guess. Thanks for your understanding.

(2) The authors rationalize existence of hexagonal tiles in the C-14 Laves phase as a result of lattice strain. However, earlier reports have suggested this tile to come from another phase, the monoclinic Mg<sub>4</sub>Zn<sub>7</sub>, which is shown to have a close similarity to the Laves phase (identical rhombic tiles), and can coexist in the same precipitates [Singh et al. 2010 PML 10.1080/09500839.2010.490049; Rosalie et al. 2010 PM 10.1080/14786435.2010.484659 )

The Mg<sub>4</sub>Zn<sub>7</sub> phase is not an approximant, but its similarity to 2D QC is seen by its unique pseudo 5f axis and a layers structure. Its closeness to the IQC has also been shown (Singh and Rosalie, Crystals 2018, 10.3390/cryst8050194 )

**Response:** We sincerely appreciate your recommendation of these valuable literatures. We have carefully read and discussed these papers. When interpreting our data before, we also considered the monoclinic  $Mg_4Zn_7$  phase. The structure is indeed similar to Laves phases and also contains hexagonal tiles and rhombic tiles. However, this kind of phase was almost only characterized in Mg-Zn-based alloys and no single  $Mg_4Zn_7$  phase is reported yet in the precipitation sequence of Al-Zn-Mg-based alloys.

In regard to the existence of hexagonal tiles of C14-Laves phase in Al-Zn-Mg alloys, before we also had referred to a related literature by [12] Chung *et al.*, An atomic scale structural investigation of nanometer-sized  $\eta$  precipitates in the 7050 aluminium alloy, *Acta Mater.*, 174 (2019) 351-368. DOI: 10.1016/j.actamat.2019.05.041. In their opinion, they concluded these hexagonal tiles in their precipitates are clearly different from  $Mg_4Zn_7$  phase. In their Page 360, they regarded the stacking faults formed from hexagonal units as antiphase boundary and further explained as below:

“Although the differently-oriented flattened hexagonal units are similar to the atomic structure of planar defects within  $Mg_4Zn_7$  reported in previous investigations, the continuously-connected flattened hexagonal units are completely inconsistent with the typical structure of  $Mg_4Zn_7$ .”

Therefore, we concluded that the appearance of hexagonal tiles cannot be simply regarded as part of  $Mg_4Zn_7$  phase. There are two more reasons in our opinion:

- (1) The  $Mg_4Zn_7$  phase is still a periodic crystalline structure with monoclinic unit but these hexagonal tiles in our precipitates are shown as nonperiodic, corresponding more to the random formation of defects. And we can hardly find one perfect  $Mg_4Zn_7$  monoclinic unit in our precipitates.
- (2) The defect bands containing hexagonal units can even be bent along different orientations (as shown in Figs. 2a and 2b), which can hardly be defined as the structure of  $Mg_4Zn_7$  phase.

These parts have been added in **Results section in Page 8, Line 4**, and all the recommended literatures are cited for discussion.

- (3) The  $MgZn_2$  hexagonal phase is not an approximant to a QC. Even its defect structure cannot be directly compared to a QC structure.

**Response:** Thanks for your comments, we totally agree that the  $MgZn_2$  hexagonal phase is not an approximant to a QC. Actually, in our manuscript, we prefer to define the precipitates as defective precipitates containing tiny quasicrystalline clusters, not a strict QC or even not an approximant QC. Here we simply report a cluster which possesses similar characteristics with quasicrystal, which is rare in the precipitation sequences of Al-Zn-Mg based alloys.

As for the comparison between QC structure and Laves phase defect structures, there are also some related investigations and publications, and we are not the first to make such a comparison.

For example: Xie et al. reported a structure as a new structured Laves phase in the Mg-In-Ca System with non-translational symmetry, compared it with traditional Laves phase and quasicrystals and defined it as an intermediate structure. ([8] Xie, *et al.*, New Structured Laves Phase in the Mg-In-Ca System with Non-translational Symmetry and Two Unit Cells, *Phys. Rev. Lett.*, 120 (2018) 085701. DOI: 10.1103/PhysRevLett.120.085701)

Yang et al. also compared the initial tiny precipitates at dislocation cores (including C14 Laves and  $\mu$  phases) with large quasicrystal precipitates at dislocation cores (showing Penrose-like random tiling structures). ([20] Yang *et al.*, Precipitation of binary quasicrystals along dislocations, *Nat. Commun.*, 9 (2018) 809-815. DOI:10.1038/s41467-018-03250-8)

Therefore, we follow up such kind of comparison between C14-Laves phase and quasicrystals in our



Al alloys systems. However, indeed, defective precipitates containing tiny quasicrystalline clusters found in our work should not be directly called as standard QC. Thus, we have kept all the descriptions of these precipitates as quasicrystalline clusters, which lose the periodic arrangement of Laves phase but have the characteristics of nonperiodic quasicrystals. As for this problem, we also made more demonstrations in Page 11-12, Line 19, copied as follows:

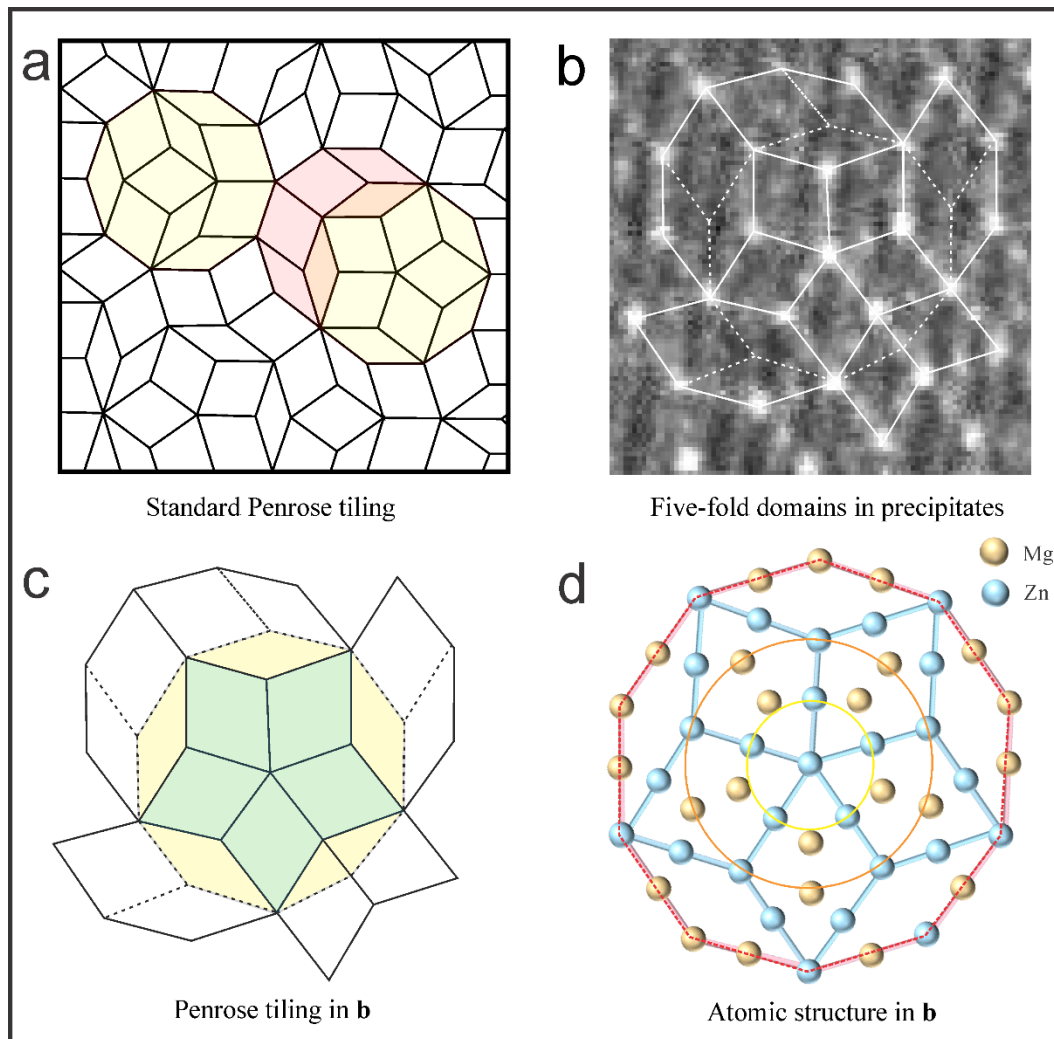
“In our work, these precipitates are likely to be designated as quasicrystalline clusters instead of standard quasicrystals or quasicrystal approximants. In previous investigations, the definitions of quasicrystals or quasicrystal approximants are strict [28, 29]. As for quasicrystal approximants, the substructures or the structural tiles are the same as those of the corresponding quasicrystals but are arranged periodically in approximants. In other words, they still possess the characteristics of periodic crystals. Consequently, “quasicrystalline cluster” is more accurate to define such tiny precipitates, and the quasicrystalline characteristics are discussed in detail below.”

(4) Figs. 5 (a- c) cannot be compared to Fig. 5 (d-f). The structures in the present study are in 2D. [Fig 5c: not a "3D stack of Penrose tiling" but a stack of "3D Penrose tiling."]

**Response:** Thank you for pointing out this. We agree with you that the structure in 2D should not be compared with a stack of 3D Penrose tiling. Therefore, as for Fig. 5, we have updated it for better illustration. Now in the new Fig. 5, we just make a simple comparison between standard Penrose tiling and precipitate structures, to demonstrate the structural similarities. Our descriptions are also revised accordingly in Page 13, Line 1, copied as follows:

“Figure 5 provides a schematic diagram of Penrose tiling in precipitates to demonstrate the similarity between five-fold structural units in the defective Laves phase precipitate and Penrose tiling.

The two-dimensional Penrose tiling has been regarded as an influential model for understanding quasicrystals' structure [30, 31], in which two types of tiles are laid down according to matching rules to form a five-fold symmetric quasiperiodic pattern. Therefore, part of standard Penrose tiling is used in Fig. 5a to describe the projection characteristics of quasicrystals [32]”. The updated Figure 5 is also shown below:



**Figure 5** Schematic diagram of Penrose tiling in precipitates. **a** Standard Penrose tiling model, typically used for understanding the two-dimensional quasiperiodic structures in quasicrystals. **b** Part of precipitates including five-fold domains. **c** Penrose tiling in **b**. **d** Atomic structure demonstration in **b** with five-fold symmetry.

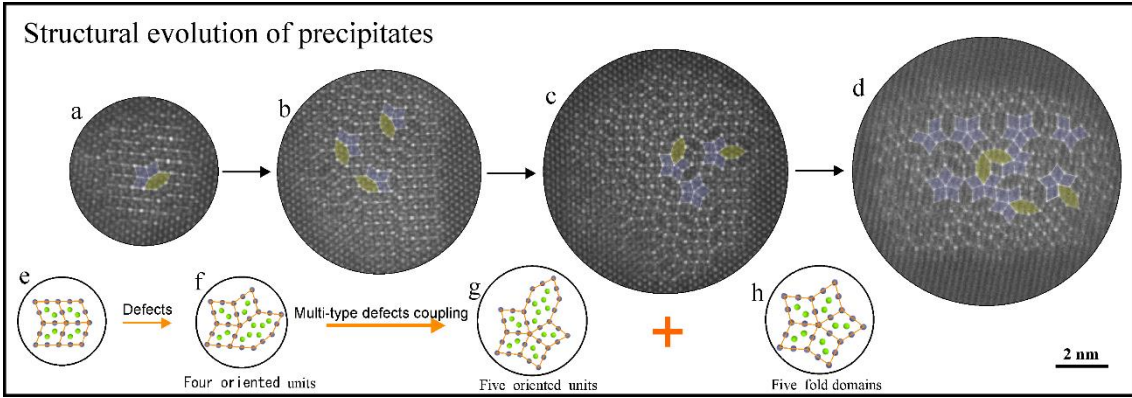
**Reviewer #2:** This paper is of high scientific quality by demonstrating the structural relationship between Laves phase and quasicrystal clusters in Al-Zn-Mg alloys at the atomic scale. The topic has been properly investigated and the paper is written with good English. The results of these HAADF-STEM images are clear and well organized, but the discussion part in the manuscript need to be improved. In this regard, considering the high quality of the journal, I suggest Minor Revision for better scientific explanation based on the following comments:

1. As for the quasicrystals in metallic alloys, many researchers have investigated and proposed similar structures defined as quasicrystal approximants. Therefore, in this paper, how to distinguish between these small precipitates, quasicrystal approximants and quasicrystals? Could you give more discussion in the manuscript according to some literatures?

**Response:** Thank you for your suggestions. In our paper, these precipitates are tiny, and we are reluctant to define them as quasicrystals or quasicrystal approximants. According to the previous reports, these structures all have their strict definition. Therefore, we prefer to define the precipitates as defective precipitates containing tiny QC clusters. We have added some discussion by citing related literatures to illustrate this problem. This part has been added in 'Results section', Page 11-12, Line 19, marked in red, and copied here as follows: "In our work, these precipitates are likely to be designated as quasicrystalline clusters instead of standard quasicrystals or quasicrystal approximants. In previous investigations, the definitions of quasicrystals or quasicrystal approximants are strict [28, 29]. As for quasicrystal approximants, the substructures or the structural tiles are the same as those of the corresponding quasicrystals but are arranged periodically in approximants. In other words, they still possess the characteristics of periodic crystals. Consequently, "quasicrystalline cluster" is more accurate to define such tiny precipitates, and the quasicrystalline characteristics are discussed in detail below."

2. The title of this paper are mainly highlighted in the word of "transformed". Although this paper has analyzed the structural relationship between C14-Laves phase with quasicrystals, the transformation process should be more clearly discussed in the discussion part to focus on the structure transformation. Detailed schematic evolution diagram is suggested to added in the discussion part.

**Response:** We totally agree with your opinion. The transformation process is detailed discussed in Page 14, Line 3, and a schematic diagram for the precipitates' evolution is added as Figure 6 in the manuscript. Figure 6 displays the detailed structural evolution during precipitate coarsening. Four different-sized precipitates from 2 nm to 5 nm are added in our updated manuscript to show the evolution process. As displayed in the first precipitate in Fig. 6a, when it is tiny (1-2 nm), initial defects can appear inside, making the standard Laves structure transform into four oriented units with three rhombic tiles and a hexagonal tile (see Fig. 6f). During precipitate coarsening, multi-type stacking faults or defects can be coupled together. Moreover, due to the special zig-zag structure of Laves phase, the rhombic tiles from Laves phase can easily transverse its growth direction by synchroshear [33], creating more possibilities for formation of five-fold symmetry structures (see Fig. 6c).



**Figure 6** Schematic diagram of structural evolution of precipitates.

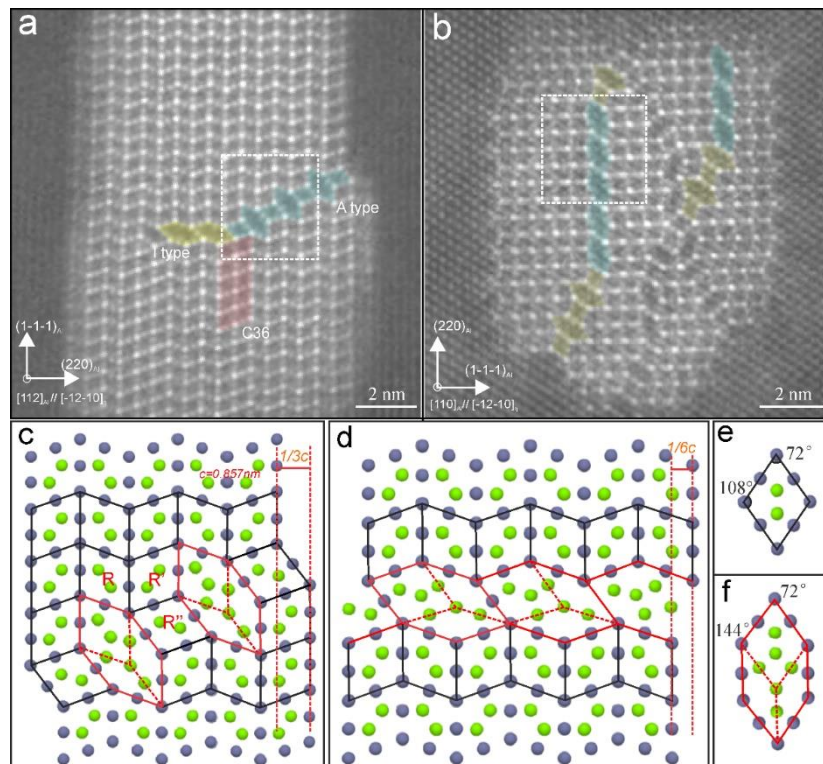
**Reviewer #3:** The manuscript presents an interesting transformation from C14 Laves phase to quasicrystalline cluster in a traditional Al-Zn-Mg alloy. The paper is based on high-quality atomic-resolution characterizations, providing some new insights about the connection between five-fold quasicrystals and crystals. Thus, I believe the paper is worth publishing. However, some questions and minor revisions are necessary before it can be accepted for publication, as listed below:  
 1. In the present work, lots of precipitates were well observed by HAADF-STEM, some are standard C14 structures while some are shown with five-fold symmetry. The main reasons for the difference should be further explained. What is the difference between these quasicrystal structures and quasicrystal approximants found in other materials?

**Response:** Thanks for your appreciation. The main reasons give rise to the five-fold symmetry structures have been further explained in updated **Figure 6** in manuscript.

As for the quasicrystals and quasicrystal approximants found in other materials, we also added some discussion by citing related literatures to illustrate this problem. **This part of discussion has been added in Page 11, Line 19, and marked in red in manuscript, copied here as follows:** “In our work, these precipitates are likely to be designated as quasicrystalline clusters instead of standard quasicrystals or quasicrystal approximants. In previous investigations, the definitions of quasicrystals or quasicrystal approximants are strict [28, 29]. As for quasicrystal approximants, the substructures or the structural tiles are the same as those of the corresponding quasicrystals but are arranged periodically in approximants. In other words, they still possess the characteristics of periodic crystals. Consequently, “quasicrystalline cluster” is more accurate to define such tiny precipitates, and the quasicrystalline characteristics are discussed in detail below.”

2. The orientation relationship between Al matrix and  $\eta$  precipitates can be more clearly marked in Figure 2.

**Response:** Thank you for your suggestions. We have updated Figure 2 (shown below) according to your advice.



3. Some small typo errors or English expressions can be corrected. For example:  
Page 14, line 19: quasi-crystalline or quasicrystalline particle? These expressions should keep consistent.  
Page 17, line 12: "c-d Schematic diagram" should be Schematic diagrams.  
Page 19, line 6: "FFT of particles" should be FFT patterns of particles.  
Please carefully check and polish again.

**Response:** Thank you for your careful check. We have revised and doubly checked them.



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S1 MgZn2 model.tif





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