

## New Structured Laves Phase in the Mg-In-Ca System with Nontranslational Symmetry and Two Unit Cells

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All of the  $AB_2$  Laves phases discovered so far satisfy the general crystalline structure characteristic of translational symmetry; however, we report here a new structured Laves phase directly precipitated in an aged Mg-In-Ca alloy by using aberration-corrected scanning transmission electron microscopy. The nanoprecipitate is determined to be a  $(\text{Mg, In})_2\text{Ca}$  phase, which has a  $C14$  Laves structure (hcp, space group:  $P6_3/mmc$ ,  $a = 6.25 \text{ \AA}$ ,  $c = 10.31 \text{ \AA}$ ) but without any translational symmetry on the  $(0001)_p$  basal plane. The  $(\text{Mg, In})_2\text{Ca}$  Laves phase contains two separate unit cells promoting the formation of five tiling patterns. The bonding of these patterns leads to the generation of the present Laves phase, followed by the Penrose geometrical rule. The orientation relationship between the Laves precipitate and Mg matrix is  $(0001)_p // (0001)_\alpha$  and  $[1\bar{1}00]_p // [11\bar{2}0]_\alpha$ . More specifically, in contrast to the traditional view that the third element would orderly replace other atoms in a manner of layer by layer on the close-packed  $(0001)_L$  plane, the In atoms here have orderly occupied certain position of Mg atomic columns along the  $[0001]_L$  zone axis. The finding would be interesting and important for understanding the formation mechanism of Laves phases, and even atom stacking behavior in condensed matter.

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A Laves phase with a chemical formula of  $AB_2$  is usually composed of the topologically close-packed (tcp) structure, in which the atoms with a smaller radius form as the close-packed planes and atoms with a larger radius embed in the tetrahedral gaps. It is reported that more than 300 kinds of Laves phases have been found in the binary alloys, and more than 900 kinds in the ternary alloys, considering the third alloying elements dissolve into the matrix [1,2]. From the viewpoint of crystalline structure, only three types of Laves structures have been frequently observed to date, including the  $C14$  structure ( $\text{MgZn}_2$ , hcp, space group:  $P6_3/mmc$ , stacking sequence:  $\cdots ABAB \cdots$ ), the  $C15$  structure ( $\text{MgCu}_2$ , fcc, space group:  $Fd\bar{3}m$ , stacking sequence:  $\cdots ABCABC \cdots$ ), and the  $C36$  structure ( $\text{MgNi}_2$  di-hcp, space group:  $P6_3/mmc$ , stacking sequence:  $\cdots ABACABAC \cdots$ ). Interestingly, the crystalline structure of the ternary Laves phase strongly depends on the alloying elements. For example, the ternary  $\text{Mg}(\text{Cu, Si})_2$  Laves phase (hcp, space group:  $P6_3/mmc$ ,  $a = 5.004 \text{ \AA}$ ,  $c = 7.872 \text{ \AA}$ ) shows a fully ordered structure, and the Mg, Cu, and Si atoms occupied the specific atomic positions [3]. In some other ternary Laves phases, such as  $\text{Mg}(\text{Cu, Al})_2$  (hcp, space group:  $P6_3/mmc$ ,  $a = 5.1 \text{ \AA}$ ,  $c = 66.7 \text{ \AA}$ ), however, the three kinds of atoms do not occupy fixed sites completely; i.e., the Mg, Cu, and Al atoms would be substituted by each other [4]. More importantly, all the Laves phases

discovered so far satisfy the general crystalline characteristic of translational symmetry.

In contrast, here we report a new structured ternary Laves phase with the  $C14$  structure precipitated in a Mg-1.5In-0.5Ca (at. %) alloy. The Laves phase has non-translational symmetry but contains two kinds of unit cells and consists of 5 types of tiling patterns on the  $(0001)_p$  basal plane. Based on the atomic-scale high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) results obtained from two vertical incident directions of  $[0001]_\alpha$  and  $[1\bar{1}00]_\alpha$ , the crystal structure of the unusual Laves phase has been systematically analyzed. These results would not only pave the way for understanding the formation mechanism of the ternary or multicomponent Laves phases in general condensed matter, but also can assist the design, calculation, and simulation of novel Mg alloys.

The Mg-1.5 at. % In-0.5 at. % Ca alloy was induction melted and solution treated at  $400^\circ\text{C}$  for 24 h, followed by aging at  $200^\circ\text{C}$  for 24 h (the alloy preparation and experimental detail are in the Supplemental Material [5]). The HAADF-STEM image in Fig. 1(a) shows numerous nanoprecipitates in the aged alloy, with the incident electron beam direction parallel to  $[1\bar{1}00]_\alpha$ . Some bright-contrast rectangular precipitates with thickness of 8–12 nm and length of 20–100 nm can be observed to distribute along the  $(0001)_\alpha$  basal plane of the Mg matrix,

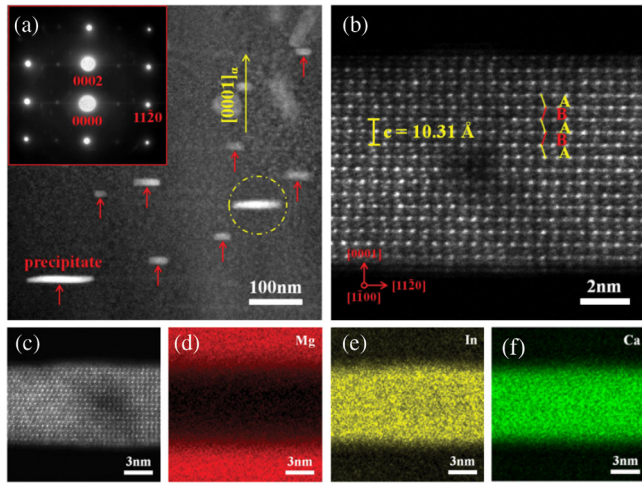


FIG. 1. HAADF-STEM images and EDS mapping results of the Mg-1.5In-0.5Ca alloy aged at 200 °C for 24 h. (a) Low-magnification HAADF-STEM image, (b) atomic-scale HAADF-STEM image, HAADF-STEM image, (c) and the corresponding EDS mapping images related to Mg (d), In (e), and Ca (f) elements. The electron beam is parallel to  $[1\bar{1}00]_{\alpha}$ .

as indicated by red arrows in Fig. 1(a). The high-resolution image of the rectangular precipitate circled in Fig. 1(a) is further displayed in Fig. 1(b). In the present Mg-In-Ca alloy, the bright dots should represent the columns enriched in In atoms, considering the fact that brightness of individual atomic columns in the HAADF-STEM image is approximately proportional to the square of the atomic numbers (the atom number is 12 for Mg, 20 for Ca, and 49 for In) [6]. In particular, the In enriched atomic columns are constituted to form arrays of  $\sim 72^\circ$  rhombus with a regular interdistance. Moreover, the precipitate exhibits a stacking sequence of  $\cdots ABAB \cdots$  along the  $[0001]_p$  direction. The characteristic crystal structure mentioned above indicates that the nanoprecipitate is in fact the Laves phase with  $C14$  structure, which is similar with the previously reported  $\beta_2'$  phase in the overaged Mg-Zn binary alloy [7–10]. And its  $c$  value of the crystal is measured to be  $\sim 10.31$  Å according to the atomic-scale HAADF-STEM image in Fig. 1(b).

The atomic-scale HAADF-STEM image and the energy dispersive x-ray spectroscopy (EDS) mapping in Figs. 1(c)–1(f) evidently shows that both the In and Ca elements are enriched in the rectangular nanoprecipitates. Moreover, the Mg elements are also observed to disperse within the precipitate. In this sense, the precipitate is determined to be a ternary Laves phase containing Mg, In, and Ca elements. Our result is in contrast to the previous report that the major precipitates observed in Mg-In-Ca alloys are the equilibrium  $Mg_2Ca$  binary Laves phase (hcp, space group of  $P6_3/mmc$ ) [11].

To accurately determine the crystal structure and the atomic coordinates of the present Mg-In-Ca ternary Laves phase, especially the atomic coordinates of the

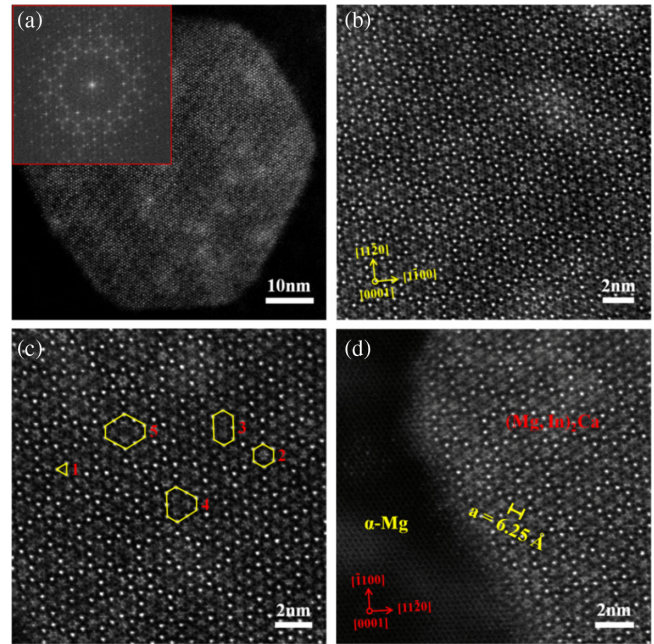


FIG. 2. HAADF-STEM images of the Mg-1.5In-0.5Ca alloy aged at 200 °C for 24 h. (a) Low-magnification HAADF-STEM image, the inset shows FFT of Fig. 2(a), and (b)–(d) atomic-scale HAADF-STEM images. The electron beam is parallel to  $[0001]_{\alpha}$ .

In element, more detailed HAADF-STEM characterizations of the Laves phase were conducted along the  $[0001]_{\alpha}$  direction, as shown in Fig. 2. The low magnification image in Fig. 2(a) displays that a hexagonal-plated precipitate with diameter of  $\sim 100$  nm lies on the  $(0001)_{\alpha}$  basal plane. The corresponding fast Fourier transformation (FFT) image of the plate precipitate is shown in top-left inset of Fig. 2(a). It can be seen that the In atoms are uniformly arranged to distribute along six regular directions on the  $(0001)_p$  basal plane, considering that the FFT pattern can only reflect crystal information of the bright-dotted In columns.

Local parts of the plate precipitate in Fig. 2(a) are enlarged and the corresponding atomic-scale images are shown in Figs. 2(b)–2(c). With the help of the Z contrast of In, it can be found that the bright-contrast In columns are arranged to form five tiling patterns. They include the (i) equilateral triangle with side length value of “a,” (ii) equilateral hexagon with side length value of “a,” (iii) narrow hexagon with side length values of “ $a + a + 2a + a + a + 2a$ ,” (iv) nonequilateral hexagon with side length values of “ $a + 2a + a + 2a + a + 2a$ ,” and (v) wide hexagon with side length values of “ $a + 2a + 2a + a + 2a + 2a$ .”

Moreover, the five tiling patterns exhibit the most three variants in the distributing orientations, and the modeled structures can be found in Figs. 3(a)–3(e). Note that the gray circle at the bottom of the modeled tiling patterns represents a unit cell of the precipitate, and the detailed atomic arrangements of the unit cells will be discussed in

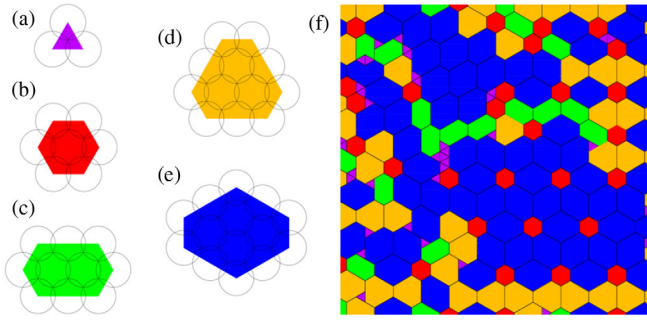


FIG. 3. Schematic diagram of (a) the equilateral triangle pattern, (b) the equilateral hexagon pattern, (c) the “ $a + a + 2a + a + a + 2a$ ” narrow hexagon pattern, (d) the “ $a + 2a + a + 2a + a + 2a$ ” nonequilateral hexagon pattern, (e) “ $a + 2a + 2a + a + 2a + 2a$ ” wide hexagon pattern, and (f) the  $(\text{Mg, In})_2\text{Ca}$  Laves phase tiling patterns.

the following. Figure 3(f) further displays the two-dimensional schematic diagram of the platelike precipitate. It can be found that the tiling patterns randomly bond together under the specific orientation and geometrical constraints following the rule of topologically close packing, and thus constitute the crystal structure of the precipitate.

Interface structure between the plate precipitate and the  $\alpha$ -Mg matrix are characterized by the high magnification image in Fig. 2(d), and the orientation relationship between them is determined to be  $(0001)_p // (0001)_\alpha$  and  $[1\bar{1}00]_p // [11\bar{2}0]_\alpha$ , which is consistent with those Laves phases previously reported in Mg alloys; i.e.,  $\beta'_2$ -MgZn<sub>2</sub> and Al<sub>2</sub>Ca precipitate [7–10,12–14]. The lattice parameter of  $a = 6.25 \text{ \AA}$  is also determined.

To further reveal the atomic arrangements of the unit cells of the Laves precipitate, the local part of the phase containing only two tiling patterns of equilateral hexagon and wide hexagon (with number ratio of 1 : 6) are specifically investigated, as viewed along the  $[0001]_p$  direction in Fig. 4(a). Based on careful observation, the corresponding atomic model of the selected area of the phase is illustrated in Fig. 4(b), including the Mg atoms indicated by blue spheres, In and Ca atoms represented by red and yellow spheres. It can be seen that the plate precipitate contains the two unit cells, the atomic arrangements of which are displayed in Figs. 4(c) and 4(d), respectively. The two-dimensional modeled unit cell 1 [Fig. 4(c)], corresponding to the area 1 in Fig. 4(a), is consisted of the In atoms in the center (represented by red spheres), the Mg atoms in the middle (represented by blue spheres), and the Ca atoms at the outside (represented by yellow spheres). Interestingly, in unit cell 2 [area 2 in Fig. 4(a)], the center, middle, and outside layers correspond to the Mg, In, and Ca atoms, respectively. In addition, three-dimensional models of the two unit cells can also be found in Figs. 4(c)–4(d). Apparently, the atomic ratio of central columns to the middle columns is 3:1. Consequently, brightness of the

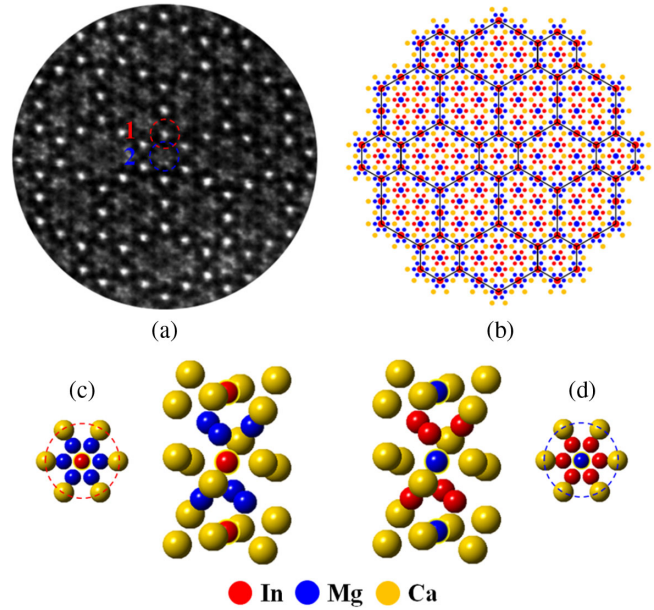


FIG. 4. (a) Atomic-scale HAADF-STEM image of the  $(\text{Mg, In})_2\text{Ca}$  Laves phase; atomic schematic diagrams of (b) corresponding modeled atomic arrangement; (c) modeled unit cell 1 marked with a red dashed circle in (a); (d) modeled unit cell 2 marked with the blue dashed circle in (a).

In atomic columns in the central column of unit cell 1 appears to be larger than that of unit cell 2. The two unit cells exhibit the same hexagonal structure, and also have the identical lattice parameters of  $a = 6.25$  and  $c = 10.31 \text{ \AA}$ .

As it is well known, since the typical feature of crystals is their rotational symmetry and translational periodicity, the atomic structure can be simply described by the repetition of one unit cell. Quasicrystals, as another important family of intermetallic compounds, have no translational symmetry, such as the icosahedral, octagonal, decagonal, and dodecagonal quasicrystals with fivefold, eightfold, tenfold, and 12-fold symmetry, respectively [15–19]. In order to describe the quasicrystal structure accurately, the Penrose tiling pattern has been widely used. It contains two types of tiling patterns, i.e., “fat”  $72^\circ$  rhombus and “skinny”  $36^\circ$  rhombus [20,21]. In the present Mg-In-Ca Laves phase, however, it has a  $C_{14}$  structure but with nontranslational periodicity, which is completely different from the discovered structures of either quasicrystals or Laves phases. The two unit cells [Figs. 4(c)–4(d)] in the present Laves phase combine with each other to form the five tiling patterns mentioned above, and finally the tiling patterns would bond together to generate the Laves phase in Figs. 1 and 2. Because of the randomness of bonding, the plate precipitate has no translational symmetry on the  $(0001)_p$  basal plane.

Finally, it is worthy to mention that the radius difference between the solvent and solute atoms plays a critical role in the formation of compounds according to the Hume-Rothery criterion. In the present Mg-In-Ca system, the atomic radius of Mg, In, and Ca is 1.60, 1.66, and 1.97  $\text{\AA}$ ,

respectively, which means that atomic radius of In is very close to that of Mg. Consequently, the In atoms would easily occupy the atomic position of Mg in the  $(\text{Mg}, \text{In})_2\text{Ca}$  Laves precipitate. However, different from the traditional view that the third element would orderly replace other atoms in a layer-by-layer manner on the close-packed  $(0001)_L$  plane, in this work, the In atoms have orderly occupied the certain positions of Mg atomic-columns along the  $[0001]_L$  zone axis. This finding is interesting and important for understanding the formation mechanism of Laves phases, more broadly, the atom stacking behaviors in condensed matter.

In conclusion, we have discovered a new precipitated  $(\text{Mg}, \text{In})_2\text{Ca}$  Laves phase with sixfold nontranslational symmetry in the as-aged Mg-1.5In-0.5Ca (at. %) alloy. Based on the atomic-scale HAADF-STEM observations along two vertical incident directions of  $[0001]_\alpha$  and  $[1\bar{1}00]_\alpha$ , the crystal structure and the atomic coordinates of the new Laves precipitates are fully unraveled. The nanoprecipitate has a C14 Laves structure (hcp, space group:  $P6_3/mmc$ ,  $a = 6.25 \text{ \AA}$ ,  $c = 10.31 \text{ \AA}$ ), but exhibits no translational symmetry on the  $(0001)_p$  basal plane, and the orientation relationship between the precipitate and  $\alpha$ -Mg matrix is determined to be  $(0001)_p // (0001)_\alpha$  and  $[1\bar{1}00]_p // [11\bar{2}0]_\alpha$ . Specifically, the two separate unit cells mentioned above combine with each other to form the five tiling patterns, and the tiling patterns bond together to generate the present Laves phase. The In atoms have orderly occupied the certain position of Mg atomic columns along the  $[0001]_p$  zone axis, which is largely different from the structures previously reported in the other Laves phases.

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