

Quasicrystal-Crystal Transformation in Zn-Mg–Rare-Earth Alloys

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We report a reversible phase transformation between the icosahedral Zn-Mg–rare-earth(RE) quasicrystal and the hexagonal crystal being not composed of any giant icosahedral atomic cluster. This clearly shows that the large atomic cluster is not an essential atomic configuration for quasicrystal formation. A structural unit of the Zn-Mg-RE icosahedral quasicrystal is suggested to be not an icosahedral atomic cluster such as the Mackay or Bergman type which have been successfully used for the structural description of the Al-based icosahedral quasicrystalline phases.

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Quasicrystals are a quasiperiodic solid exhibiting rotational symmetries forbidden to ordinary crystals, in which the atoms are arranged nonperiodically [1,2]. To understand the real atomic structure, Elser and Henley showed that, according to the projection scheme, some cubic crystals composed of large atomic clusters with icosahedral (*i*) symmetry can be viewed as variant structures of quasicrystal [3]. In the sense that they are generated by strip slopes with rational approximations of $\tau [= (1 + \sqrt{5})/2]$, the crystals are referred to as *approximant* crystal. Although the scheme is mathematical, it implies a realistic picture on how the quasicrystals form; the noncrystallographic symmetry of the robust *i*-atomic clusters forces their nonperiodic arrangement, leading to formation of quasicrystal. In fact, quasicrystalline phases are formed in rapidly solidified alloys with compositions close to those of the *approximant* crystals [4]. Besides, a reversible quasicrystal–*approximant* crystal transformation was reported for the stable *i*-AlCuFe phase [5]. These lead to an established concept that the quasicrystal is essentially a cluster-based structure, and thus new quasicrystal discoveries have been aided by a search for crystalline phases composed of large *i*-atomic clusters.

The stable face-centered (*F*-type) *i*-quasicrystal in the Zn-Mg-RE system reveals a high structural perfection [6] comparable to or better than that of the *i*-AlCuFe which is known as one of the best quasicrystalline phases. A preliminary single-crystal x-ray experiment indicated that the *i*-ZnMgRE has a novel atomic structure which is significantly different from those of the *i*-Al–transition-metal(TM) quasicrystalline phases [7]. To determine the structure, it is indispensable to know which crystalline phase is in close relation in atomic structure. In terms of this, we have recently found two-dimensionally inflated hexagonal superstructures (all belong to $P6_3/mmc$) [8] in the vicinity of the stoichiometry *i*-Zn₆Mg₃RE₁ [9]. These crystals are not expected from the projection scheme because it allows only partial groups of $m\bar{3}\bar{5}$ (*i*-symmetry), such as the point group *m3* (cubic) or *mmm* (orthorhombic) to be the *approximant* crystal. Further, although the electron diffraction features can be related to an *i* sym-

metry by twinning operation [10], no giant *i*-atomic cluster can be defined in these hexagonal structures; only the nearest 13 atoms form a distorted icosahedron [11,12]. These facts are in sharp contrast to the case of stable *i*-Al-TM phases, for which the cubic *approximant* crystals built of various size of *i*-atomic clusters have been systematically found (typical examples are summarized in [13]). With these in mind, one may suspect that the atomic structures of the Zn-Mg-RE hexagonal phases would provide available information for the *i*-ZnMgRE structure.

In this Letter, we demonstrate strong evidence that the hexagonal structure is closely related to the *i*-ZnMgRE quasicrystal structure; a reversible as well as an irreversible hexagonal–quasicrystal phase transformations is shown. This is the first observation of a reversible transformation between the *i* quasicrystal and the crystal which does not contain any large *i*-atomic clusters. A structural unit of the *i*-ZnMgRE is suggested to be not giant *i*-atomic clusters which are currently believed to be essential for building quasicrystalline structure. With this aspect, we discuss the high-resolution transmission electron microscope (HRTEM) image contrasts of the *i*-ZnMgRE as compared with the three-dimensional Penrose tiling (3DPT).

Samples used for the present study are Zn₆₀Mg₃₀Sm₁₀, Zn₆₀Mg₃₀Y₁₀, and Zn₆₅Mg₂₅Y₁₀ alloys (see Ref. [8] for details of preparation). For identification of the phases, transmission electron microscopy (TEM), x-ray diffractometry with a CuK α (XRD), and scanning electron microscopy (SEM) equipped with energy-dispersive x-ray spectroscopy (EDS) were used. Conventional ZAF (Z: atomic number; A,F: absorption and fluorescence correction factors, respectively) correction was made to obtain reliable compositions, resulting in typical errors of ± 1.5 , ± 3.0 , ± 0.5 at. % for Zn, Mg, and Y, respectively. HRTEM images were obtained by a 400 kV TEM with a resolution of 0.17 nm.

As discussed empirically in the previous work [6], formation of the stable *i*-ZnMgRE phase is dominated by the atomic diameter of the RE elements. It was found that Sm(3.60 Å)/Y(3.55 Å) corresponds to the threshold

boundary in terms of formation of stable *i* phase. In the slowly solidified $Zn_{60}Mg_{30}Sm_{10}$ alloy, the hexagonal phase with $a = 14.6 \text{ \AA}$ and $c = 8.8 \text{ \AA}$ denoted as hex-ZnMgRE phase is obtained as almost a single phase [10]. Figures 1(a)–1(c) show the TEM micrographs and selected-area electron diffraction (SAED) patterns of a rapidly solidified (RS) $Zn_{60}Mg_{30}Sm_{10}$ alloy. It is clear that the hex-ZnMgSm phase can form the *i*-quasicrystalline phase [primitive icosahedral lattice (*P* type) known from Fig. 1(c)] in spite of no large *i*-atomic clusters in the structure. We note that there is no trace of second phase at the grain boundaries, suggesting a complete single *i* phase with a reasonable stoichiometry.

Next, we show a reversible phase transformation between the *i*-ZnMgY and the hex-ZnMgY in the vicinity of $Zn_6Mg_3Y_1$. We found that, for the $Zn_{65}Mg_{25}Y_{10}$ alloy, the reversible transformation is accomplished with a quite small compositional change. Figures 2(a) and 2(b) show the SEM micrographs of the annealed (873 and 773 K) $Zn_{65}Mg_{25}Y_{10}$ alloys. It can be confirmed from these micrographs that the volume fractions of the major phase are more than 90%, although both the alloys contain few minor phases indicated in the figures. As shown by the SAED patterns inserted in Figs. 2(a) and 2(b), the dominant phase at 873 K is the *i*-ZnMgY (*F* type), while that below 773 K is the hex-ZnMgY phase. This is also confirmed by powder x-ray diffraction patterns shown in Fig. 2(c). Since the single *i*-ZnMgY phase is obtained at a lower temperature (750 K) for the $Zn_{60}Mg_{30}Y_{10}$ alloy [9], the single *i*-phase region is considered to shift at high temperatures and the hex phase is a compound adjacent to the *i* phase at low temperatures. Further details of the phase equilibria will be discussed elsewhere. The phase distributions in Figs. 2(a) and 2(b) were confirmed to be reproduced by subsequent annealing of the alloys (873 K \leftrightarrow 773 K), confirming the reversible

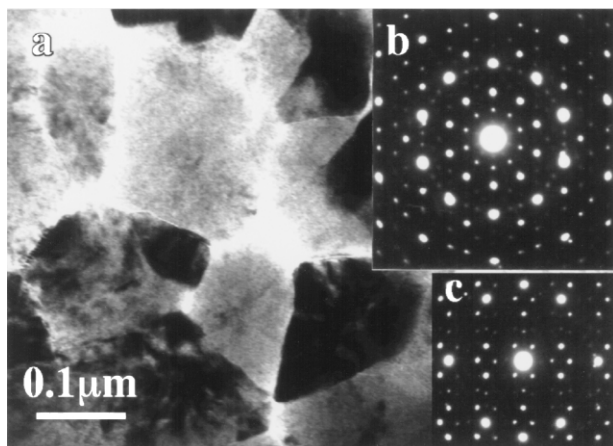


FIG. 1. (a) TEM micrograph of a rapidly solidified $Zn_{60}Mg_{30}Sm_{10}$ alloy. The selected area electron diffraction patterns obtained from the grains in (a), showing the (b) fivefold and (c) twofold symmetries of the icosahedral phase.

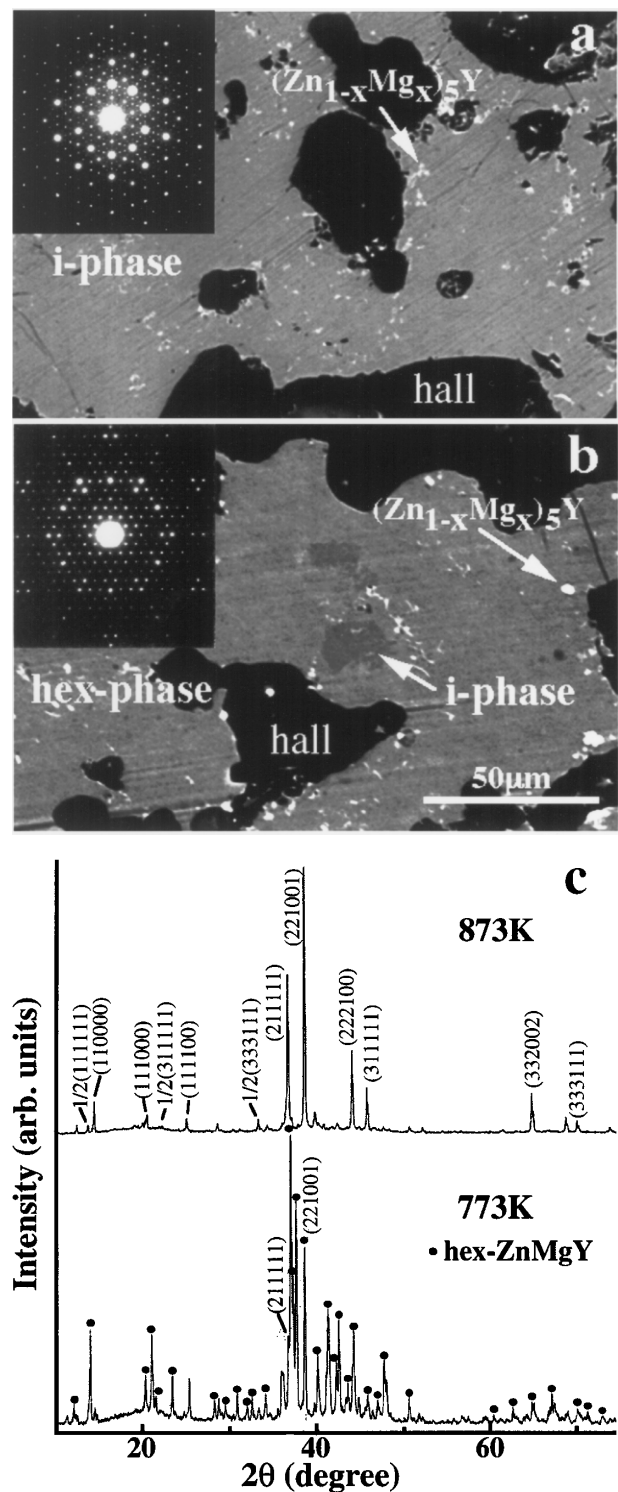


FIG. 2. SEM micrographs showing the component phases of the $Zn_{65}Mg_{25}Y_{10}$ alloy annealed at (a) 873 K for 20 h and (b) 773 K for 72 h. The electron diffraction patterns of the major phase of (a) and (b) are inserted. The small white particles in (a) and (b) are the $(Zn_{1-x}Mg_x)_5Y$ compound with $x = 0.1-0.2$. The dark gray region in (b) corresponds to the *i*-ZnMgY phase. (c) Powder x-ray diffraction patterns of the alloys (a) and (b), in which the major reflections are indexed with the face-centered icosahedral quasicrystal (upper) and the hexagonal crystal [11,12] (lower).

i-ZnMgY–hex-ZnMgY transformation. The compositions of the phases were determined to be approximately *i*-Zn₆₄Mg₂₇Y₉ (873 K) and hex-Zn₆₆Mg₂₇Y₇ (773 K), respectively. We especially note that the compositional difference between the phases is quite small.

We have shown clearly that the *i* phase is a metastable product of the hex phase in the Zn₆₀Mg₃₀Sm₁₀ alloy. Further, the reversible *i*-hex phase transformation has been accomplished with an extremely small compositional change in the Zn₆₅Mg₂₅Y₁₀ alloy. These strongly indicate a similar local atomic configuration of these phases. Since there is no giant *i*-atomic cluster in the hex phase, it is evident that the giant *i*-atomic cluster is not an essential factor for formation of quasicrystals. A structural unit of the *i*-ZnMgRE quasicrystal is probably not the *i*-atomic cluster such as the Mackay or the Bergman type which have been successfully used for the structural description of the *i*-quasicrystalline phases. With this in mind, we discuss the HRTEM image contrasts of the *i*-ZnMgRE.

Figures 3(a)–3(c) show HRTEM images of the *i*-ZnMgY phase taken with the incident beam parallel to the fivefold axis. The images with different resolutions were obtained under different imaging conditions. In the nearly best resolution image of Fig. 3(a), a so-called structure image [14], decagon contrasts composed of a bright ring decorated by ten bright dots (hereafter denoted as *D*-contrasts) can be seen, as exemplified by the circle. Apparent features of this image are quite similar to those observed in the *i*-AlMnSi and *i*-AlLiCu [14], and the *D*-contrasts were attributed to the Mackay or the Bergman atomic clusters with icosahedral symmetry. Figure 3(b) was taken from the same region of Fig. 3(a) with larger defocus value to obtain lower resolution, which is caused by a change of major diffracted beams contributed for imaging (a phase difference between direct and diffracted beams is changed by a focus value in HRTEM, which can be used as a filtering technique to select a desired diffracted beam to be a major contribution for imaging

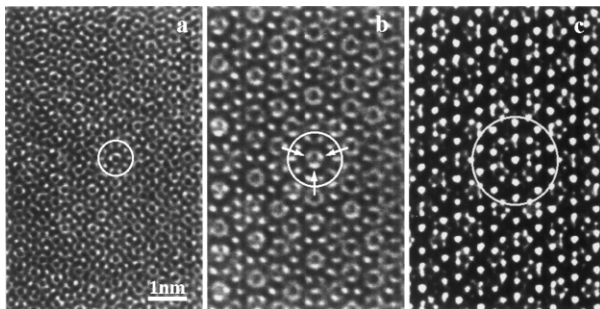


FIG. 3. HRTEM images of the *i*-ZnMgY obtained from cleavage grains of the Zn₆₀Mg₃₀Y₁₀ alloy (annealed at 750 K for 100 h), taken with (a) thin crystal (less than 10 nm) under nearly the Sherzer defocus (−45 nm for the present TEM) (b) thin crystal (less than 10 nm) under larger defocus value ≈ -80 nm (c) thick crystal (more than 10 nm) under nearly the Sherzer defocus.

[15]). Interestingly, in Fig. 3(b) the τ scaled up *D*-contrasts indicated with a circle emerge from the image, in which the inner ring shows triangle contrasts modulations as indicated by arrows. Figure 3(c) is a lattice image reflecting the quasilattice of the *i*-ZnMgY, revealing larger decagonal linkage of the dots.

Although the features of image contrasts can be interpreted in terms of the three-dimensional arrangement of *i*-atomic clusters, we emphasize that the self-similar inflation seen in Figs. 3(a)–3(c) can simply be interpreted by the 3DPT projected along the fivefold axis, as shown in Fig. 4(a). As indicated by arrows, triangle modulations are expected to appear naturally in the 3DPT, indicating that a simple atomic decoration of the 3DPT can produce the image contrasts seen in Figs. 3(a)–3(c) (the modulation can also be explained by the *i*-atomic cluster description due to superimposing projection of the *i* clusters in the image [16]). This means that the HRTEM images with the *D*-contrasts cannot be a conclusive evidence of the giant *i*-atomic cluster picture, since for the *i*-quasicrystal the image contrasts reflect the projected 3D quasiperiodic atomic structure. It should be kept in mind that, even by the diffraction method, it is quite difficult to conclude on this matter due to the isomorphic nature of quasilattice [17]. Because of these, the *approximant* crystals have provided indirect but strong evidence of the *i*-atomic cluster description of the *i*-quasicrystal structures.

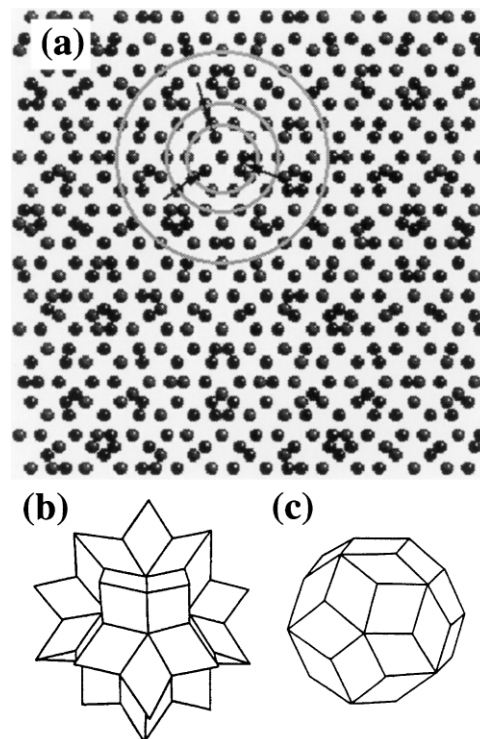


FIG. 4. (a) Vertex positions of the three-dimensional Penrose tiling projected along the fivefold axis. (b) the stellate zonohedron (SZ), and (c) the rhombic triacontahedron (RT) defined in the three-dimensional Penrose tiling.

In the atomic model based on the τ^3 inflation, the symmetric *i*-atomic clusters are defined for the stellate zonohedron [SZ, Fig. 4(b)] and rhombic triacontahedron [RT, Fig. 4(c)] in the 3DPT [18]. Again, this is based on an assumption that the giant *i*-atomic clusters in the *approximant* crystal also exist in the *i* quasicrystal. Since there are only the smallest icosahedra with 13 atoms (distorted) in the corresponding crystalline phase of the *i*-ZnMgRE, it is reasonable to presume that the symmetric atomic decoration is not imposed upon the RT interior; the RT is a polyhedron with *i* symmetry on external shell but its interior breaks the *i* symmetry in the 3DPT (the SZ is a unique polyhedron with perfect *i* symmetry). Thus, the τ^3 inflation with the *i*-atomic cluster concept is not essentially needed for the *i*-ZnMgRE atomic structure, leading to an individual atomic decoration of the 3DPT.

It is worth mentioning here that a decagonal (*d*-) ZnMgRE quasicrystal has recently been shown to have a simple structure in which the atomic arrangement in the tenfold symmetry plane can be interpreted as the Penrose tiling decorated by individual atoms [19]. This is consistent with the structural discussion on the *i*-ZnMgRE structure done above. For a structural description of the *d*-ZnMgRE, a new concept of *quasi-unit-cell* [20] has been successfully applied instead of the symmetric atomic cluster picture. For *d* quasicrystals, the *quasi-unit-cell* is defined as a non-tenfold symmetric decagonal unit (should be energetically favorable in terms of given elements) that can overlap with neighbors. This reminds us that the *quasi-unit-cell* description can also be applied for the *i*-ZnMgRE by assuming a certain icosahedral unit in the 3DPT, which does not reveal *i* symmetry. In terms of this, a question has arisen on the structure of *i*-Al-TM phases of whether the *i*-atomic clusters are actually symmetrical or not [21]. This may be related to the *quasi-unit-cell* concept, and the *i*-atomic cluster without *i* symmetry should not correspond to the SZ but to the RT of the 3DPT.

In summary, we have shown the reversible hexagonal crystal-*i*-quasicrystal transformation in the Zn-Mg-RE alloys. Since there is no giant atomic cluster with *i* symmetry in the hexagonal crystal, the results strongly suggest that the *i*-atomic clusters, such as the Mackay or Bergman type currently believed to be building blocks of the quasicrystal structure, are not an essential atomic configuration for constructing the quasicrystals. Instead, the energetically favorable *quasi-unit-cell* concept could

be applied; an energetic that may naturally force a similar local atomic environment between the quasicrystal and the corresponding crystal. This structural reinterpretation will be a key to understanding why the quasicrystals form.

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