Structure of a Quasicrystal without Atomic Clusters

Eiji Abe, Taku J. Sato, and An Pang Tsai

National Research Institute for Metals, 1-2-1 Sengen, Tsukuba 305, Japan

(Received 23 March 1998)

We show that, using high-resolution transmission electron microscopy, the first Frank-Kasper decagonal quasicrystal discovered in Zn-Mg-rare-earth alloys has a novel atomic structure in which the atomic arrangement in the tenfold symmetry plane can simply be interpreted as the Penrose tiling decorated by individual atoms. This is in sharp contrast to the idea of linking atomic clusters which have the same point symmetry as the Fourier spectrum of quasicrystals, which has been successfully used to describe the structure of quasicrystals until now. An energetically favorable *quasi-unit-cell* concept is applied for the structural description. [S0031-9007(99)09558-7]

PACS numbers: 61.44.Br, 61.16.Bg, 61.66.Dk

Quasicrystals, which exhibit icosahedral, decagonal, and other symmetries forbidden to ordinary crystals, have now been firmly established as a new form of solid. Nonperiodic structural features displayed by a quasilattice have been well explained by the Penrose pattern, a tiling of two different tiles arranged with complicated matching rule [1,2]. To understand the real atomic structure of the quasicrystals, Elser and Henley showed that large atom clusters with icosahedral symmetry, referred to as Mackay and Frank-Kasper type, exist in some crystals (approximant), and gave a simple interpretation of their periodic and quasiperiodic arrangements (quasilattice) according to the projection method [3]. This idea implies that the noncrystallographic symmetry of the atom cluster forces their nonperiodic arrangement, leading to formation of quasicrystals. A high-structural perfection of thermodynamically stable quasicrystals is currently believed to be due to a robustness of the symmetric atomic clusters.

Generalized Penrose patterns with different local tiling features show quite similar diffraction intensity distributions [4], which are produced using the *projection method* by changing the window shape and position. Besides, a quasilattice is locally isomorphic by nature. Therefore it is difficult to determine the cluster-based quasicrystal structure using diffraction method, and thus a direct structural observation has been essentially required for quasicrystals. Indeed for the decagonal (d) quasicrystal, the structure is described in terms of a two-dimensional quasiperiodic lattice plane so that the high-resolution transmission electron microscopy (HRTEM) along the tenfold symmetry axis directly reflects the quasiperiodic arrangement of atoms. So far, based on HRTEM studies, *d*-atom clusters with various sizes have been defined both in thermodynamically stable and metastable d phases in Al-transition-metal (TM) alloys [5]. Among the d quasicrystals reported, the *d*-AlNiCo phase with a primitive structure is regarded as one of the best samples showing a long-range quasiperiodic order [6]. The structure is explained well by a d cluster with a 20 Å diameter [7-9](hereafter, denoted as DAINiCo-cluster) with an arrangement as in the pentagonal Penrose tiling.

Recently, we have discovered a new d quasicrystal in Zn-Mg-rare-earth (RE) alloys, whose structure should be classified as the first Frank-Kasper type [10]. Here we present a preliminary structural model of this new phase based on HRTEM study, which shows that this structure is significantly different from that of the d-AlTM phases. The structure is the first example of a d-quasicrystal structure without any d clusters.

Zn₇₀Mg₂₀Dy₁₀ (annealed at 620 K for 60 h) alloy was used for studying the d phase, in which several phases coexist. The composition of the *d*-phase was determined to be $Zn_{58}Mg_{40}RE_2$ [10]. The phase is thermodynamically stable and shows high structural perfection which is comparable to the best *d*-AlNiCo; neither diffuse streaks nor superlattice reflections in the diffraction patterns [11]. A related crystalline phase with Zn7Mg4 type structure was observed in the Zn₆₀Mg₃₈Dy₂ alloy annealed at higher temperature (723 K), whose composition was approximately Zn₆₆Mg₃₂Dy₂ [10]. The HRTEM images were obtained at 400 kV with a Jeol JEM-4000EX TEM having a point-to-point resolution of 0.17 nm. Samples for TEM observation were prepared by dispersing crushed alloys on perforated carbon films supported on copper grids. Simulation of image contrasts was performed on the TEMPAS program whose calculation is based on multislice method.

The tenfold symmetry diffraction pattern of the d-ZnMgRE phase was shown to be analogous to that of the *d*-AlNiCo with a ratio of the unit vector length, $a_{\rm ZnMgDy}/a_{\rm A1NiCo}$, approximately 0.7 [11]. This indicates a structural similarity of both the d phases, and hence in the d-ZnMgRE one may expect an existence of a d-atom cluster analogous to the D_{A1NiCo} cluster. However, the present HRTEM study showed that there is no such cluster in the *d*-ZnMgRE. Figure 1(a) shows the HRTEM image of the d-ZnMgDy, taken along the tenfold axis under nearly the Sherzer defocus (-45 nm for the present)400 kV TEM). This is a so-called structure image which reflects the projected potential of atomic arrangements; atom positions reveal dark contrasts. Under a similar imaging condition for the d-AlNiCo, the D_{A1NiCo} cluster was characterized by a linkage of ten ring contrasts which



FIG. 1. HRTEM images of the *d*-ZnMgRE quasicrystals formed in the $Zn_{70}Mg_{20}Dy_{10}$ alloy. The images were obtained from cleavage grains at (a) thin region where near edge with nearly the Sherzer defocus and (b) thick region with a larger defocus than the Sherzer one. In (b), Fourier diffractogram of the image is inserted at upper right side.

were attributed to the decagonal atomic columns with nearest-neighbor atoms [7]. In Fig. 1(a), a similar decagonal unit denoted as D unit (about 14.5 Å in diameter) can be defined, as exemplified by white circles. The D units are connected by sharing two small ring contrasts, forming a pentagonal arrangement. These features are analogous with those observed in the d-AlNiCo. However, it should be noted in particular that the interior contrasts of the D units do not exhibit tenfold symmetry [details are seen in Fig. 3(d)]. Thus, the D unit is not an atomic cluster with tenfold symmetry. This is seen clearly in the lower resolution HRTEM image of Fig. 1(b), in which the corresponding D units are represented by connecting white dots with an interval of about 4.5 Å. The Fourier diffractogram inserted confirms that the observed region has an overall tenfold symmetric structure. Inside every D unit, four dots form a rhombus, breaking the tenfold symmetry. Because of this arrangement, an extra D unit can be drawn inside the pentagonal arrangement of the Dunits, which is also shown in Fig. 1(b). We note that this D unit is a deformed decagon with a dot that is displaced out of the linkage. This feature will be discussed later (Fig. 4). From these facts, it is evident that the structure of the *d*-ZnMgRE can be interpreted to be an arrangement of dots connected at an interval of 4.5 Å, and not by large d-atom clusters.

A crystal structure close in structure to the *d*-ZnMgRE is the Zn₇Mg₄ phase. In this structure, shown in Fig. 2(a) [12], a pentagonal arrangement of atoms exists in the plane (y = b/2), which partially forms edge-sharing tiling as drawn by a black line. For each pentagon, an inverted atomic pentagon is located in the lower layer (y = 0) sandwiching an atom at an icosahedral center, forming an icosahedral (*i*) atomic column [11]. Distances between the *i*-atomic columns connected by edge-sharing pentagons are in the range of 4.51-4.64 Å. Figure 2(b) shows a



Zn : $\bigcirc y=0$, $\bigcirc y=b/2$, $\bigcirc y=b/4$ and (3b)/4 layer Mg : $\bigcirc y=0$, $\bigcirc y=b/2$ layer

FIG. 2. (a) [010] projection of the Zn_7Mg_4 monoclinic structure. Rhombuses drawn by dashed lines represent a structural unit of Cu₂Mg type Laves phase. (b) HRTEM image of the $Zn_{66}Mg_{32}Dy_2$ phase with Zn_7Mg_4 type structure, taken along the [010] zone axis. Simulated image (-70 nm defocus and 10 nm thickness) with atomic projection is inserted at right-hand side. The arrangement of pentagons formed by atoms, drawn in (a), appears as that of white dots drawn by white lines in (b).

HRTEM image corresponding to Fig. 2(a), together with the simulated image. This was taken under a condition similar to that of Fig. 1(b). By comparison of the observed and the calculated images, it is known that the *i*-atomic columns are imaged as white dots. Thus, the dots with 4.5 Å interval in Fig. 1(b) can be interpreted by a similar atomic configuration as that in the Zn₇Mg₄ structure. Based on this, we propose an atomic structural model corresponding to the D units drawn in Fig. 1. This is shown in Fig. 3(a). Atoms at the z = c/4 and 3c/4 characterize a tetrahedrally packed nature of Frank-Kasper phase. We note that a part of this atomic configuration is realized by a slight displacement of atoms of the pentagonal linkages in the Zn₇Mg₄ structure indicated in Fig. 2(a). Calculated images based on the model shown in Figs. 3(b) and 3(c), reproduce well the observed image contrasts for different imaging conditions of Figs. 3(d) and 3(e), respectively, confirming the validity of the model. In the model, atoms in the z = 0 and c/2 planes are placed at different vertices of the Penrose tiling, which are generated by the section method using pentagonal occupation domains with an inverse relation. This is responsible for the overall tenfold symmetry and the space group of $P10_5/mmc$ with a 10_5 screw operation [4,13]. It is reasonable to assume that the short-diagonal vertices of the thin rhombi are half-occupied with a constraint of forming deformed pentagons shown in Fig. 3(a) (with its columnar configuration, this corresponds to an interpenetrated connection between the neighboring *i*-atomic columns). We note in particular that these deformed atomic pentagons in fact exist in the Zn₇Mg₄ structure, and a similar configuration can be found in a computer-simulated structural model [14], supporting strongly the present assumption. A displacive disorder induced by the occupational disorder of the halfoccupied sites may give rise to a diffuse scattering in the tenfold plane.



FIG. 3. (a) Preliminary atomic structure model for the d-ZnMgRE and the pentagonal arrangement of atoms in the structure. Edge length of the Penrose tiling is 1.74 Å. Example of ambiguous sites of the thin Penrose rhombi are shown by light circles for the upper part, in which one of the pairs is indicated by arrows. Atomic distances in the model agree with those in the Zn₇Mg₄ structure (Zn-Zn:2.57-2.68; Zn-Mg:3.09-3.12; Mg-Mg:2.7-3.8 Å). Simulated images based on the model with defocus and thickness (b) -40 and 3 nm and (c) -70 and 10 nm, respectively. These were calculated assuming a binary Zn-Mg phase; atom sites in z = c/4 and 3c/4 layers are all occupied by Zn, while each of those in z = 0 and c/2 layers are occupied by Zn and Mg with equal probability, 0.5, resulting approximate composition Zn_6Mg_4 . (d), (e): Enlargements of observed contrasts of D unit in Figs. 1(a) and 1(b), respectively.

This structural description leads to a conclusion that the atomic arrangement in the plane is characterized by a pentagonal (deformed) network. However, an averaged structure should be interpreted as the rhombic Penrose tiling formed by individual atoms. This agrees with the fact that the tenfold diffraction feature of the d-ZnMgDy resembles the calculated diffraction intensity of the Penrose pattern very well [4,11]. We emphasize that the present simple description of the d-ZnMgRE structure is in stark contrast to those of the stable d-AlTM quasicrystals whose structure has been successfully described by separated tenfold or fivefold symmetric atom clusters connected by linkages which form the corresponding quasilattice.

The structural features described by the D units, shown in Figs. 1(a) and 1(b), are simply explained by the pentagonal Penrose tiling shown in Fig. 4(a). It can easily be imagined that the pentagonal Penrose pattern corresponds to a simplified sketch of the pentagonal atomic arrangement in the tenfold plane (Fig. 3). As indicated by dashed lines, the D units can be drawn to form a pentagonal arrangement by edge-sharing connection. One notices that an extra incomplete D unit naturally comes out, which originates from three symmetry-breaking pentagons inside the D unit [we note that "matching rule" is not maintained for the region indicated in Fig. 1(b)]. It is noteworthy here that, by specifying the TM atom positions, the D_{A1NiCo} cluster was shown to be not tenfold symmetric [15] with the same fashion of Fig. 4(a). On this basis, a new d-AlNiCo structural model was constructed by decomposing the D_{A1NiCo} cluster into smaller atom clusters, *P* and *S* type [15] which exist in the $Al_{13}Fe_4$ crystal (very recently, the symmetry breaking of the D_{A1NiCo} cluster was interpreted by a chemical disordering [16]. This critical issue of d-AlNiCo will be discussed in detail [17]). This new *d*-AlNiCo model has recently been modified according to a *quasi-unit-cell* concept [18] which defines a nontenfold symmetrical decagonal unit that can overlap with neighbors by sharing atoms in a well-defined way [19], resulting in uniquely a perfect Penrose tiling. Considering the simple atomic structure of the present d-ZnMgRE phase, the possible quasi-unit-cell is immediately defined [Fig. 4(a)]. In fact, for the HRTEM image of the *d*-ZnMgRE showing characteristic decagon ring contrasts without tenfold symmetry (about 2.3 nm diameter; τ times larger than the D unit) [20], overlap tiling can be drawn in terms of the A and B overlaps [19], as shown in Fig. 4(b). This realizes the perfect Penrose tiling as a real atomic structure from an atomic scale to a macroscopic scale for the *d*-ZnMgRE.

Now we note that the structural difference between the d-ZnMgRE and d-AlNiCo is systematically understood by their corresponding crystalline phases. That is, the P and S clusters [15] in the Al₁₃Fe₄ structure are extended to next-nearest atoms, while the *i*-atomic column in the Zn₇Mg₄ structure is formed by the nearest-neighbor atoms. This causes the similar tiling feature with different edge lengths and thus the different *quasi-unit-cell* structures of both the d phases, resulting in the analogous tenfold diffraction patterns [11]. These facts strongly suggest that the local atomic structure of the quasicrystal should be derived from the related crystalline phase at the close composition. This seems to be consistent with a scheme that the atomic arrangement in the quasi-unit-cell should be energetically favorable in terms of given elements.

In conclusion, we have shown that the d-ZnMgRE has a simple structure described by a Penrose tiling decorated by individual atoms—the simplest realization of the



FIG. 4(color). (a) A part of the pentagonal Penrose tiling and the quasi-unit-cell with semitransparent kite decorations. Decagonal linkages formed by ten pentagons are represented by dashed lines. (b) HRTEM image of the d-ZnMgDy taken at relatively thicker region than that of Fig. 1(a), in which the center of *i*-atomic column appear to be bright spots (confirmed by simulation with 6 nm thickness). Several decagonal rings corresponding to the quasi-unit-cells are traced by red lines, and the D unit is shown by yellow lines in the enlarged quasi-unit-cell inserted at right-hand side. Note that the decagons overlay one another in two discrete ways, A and B type [18,19].

Penrose tiling as a real atomic structure. This is the first example of a quasicrystal structure without any symmetric atomic clusters which have been believed to be essential for quasicrystal formation and successfully used to describe the quasicrystal structure. Instead, a energetically favorable quasi-unit-cell is applied for the structural description. This structural reinterpretation may lead to a better understanding of why the quasicrystal forms.

We thank P. J. Steinhardt for valuable advice regarding the overlap tiling. This work has been supported by Core Research for Evolutional Science and Technology, Japan Science and Technology Corporation.

- [1] R. Penrose, Bull. Inst. Math Appl. 10, 266 (1974).
- [2] D. Levine and P.J. Steinhardt, Phys. Rev. Lett. 53, 2477 (1984).
- [3] V. Elser and C. L. Henly, Phys. Rev. Lett. 55, 2883 (1985); C. L. Henley and V. Elser, Philos. Mag. B 53, L59 (1986).
- [4] K. N. Ishihara and A. Yamamoto, Acta Crystallogr. Sect. A 44, 508 (1988); A. Yamamoto and K. N. Ishihara, Acta Crystallogr. Sect. A 44, 707 (1988).
- [5] K. Hiraga, in Advances in Imaging and Electron Physics, edited by P.W. Hawkes (Academic Press, New York, 1998), p. 37.

- [6] S. Ritch *et al.*, Philos. Mag. Lett. **74**, 99 (1996); A.P. Tsai *et al.*, Philos. Mag. Lett. **74**, 233 (1996); D. Joseph, S. Ritch, and C. Beeli, Phys. Rev. B **55**, 8175 (1997).
- [7] K. Hiraga, W. Sun, and A. Yamamoto, Mater. Trans. JIM 35, 657 (1994).
- [8] W. Steurer and K. H. Kuo, Acta Crystallogr. B 46, 703 (1990).
- [9] S.E. Burkov, Phys. Rev. Lett. 67, 614 (1991).
- [10] T.J. Sato, E. Abe, and A.P. Tsai, Philos. Mag. Lett. 77, 213 (1998).
- [11] E. Abe, T.J. Sato, and A.P. Tsai, Philos. Mag. Lett. 77, 205 (1998).
- [12] Ya. P. Yarmoryuk, P. I. Kripyakevich, and E. V. Mel'nik, Soviet Phys. Crystallogr. 25, 329 (1975).
- [13] A.L. Mackay, Physica (Amsterdam) 114A, 609 (1982);
 T. Janssen, Acta Crystallogr. Sect. A 42, 261 (1986).
- [14] J. Roth and C.L. Henely, Philos. Mag. A 75, 861 (1997).
- [15] K. Saitoh et al., Jpn. J. Appl. Phys. 36, L1404 (1997).
- [16] Y. Yan, S.J. Pennycook, and A.P. Tsai, Phys. Rev. Lett. 81, 5145 (1998).
- [17] E. Abe et al. (to be published).
- [18] P.J. Steinhardt et al., Nature (London) 396, 55 (1998).
- [19] P. Gummelt, Geometriae Dedicata 62, 1 (1996); P.J. Steinhardt and H.-C. Jeong, Nature (London) 382, 433 (1996).
- [20] E. Abe, T.J. Sato, and A.P. Tsai, in *Proceedings of the International Congress on Electron Microscopy14, Cancun* (IOP, Bristol, 1998), Vol. III, p. 23.