

Orthorhombic τ -Zn–Mg–Dy phase related to a Frank-Kasper type decagonal quasicrystal

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We report a novel Zn–Mg–Dy phase, denoted as the τ -phase, whose structure is related to that of the Frank-Kasper type decagonal Zn–Mg–Dy phase, based on electron diffraction and high-resolution transmission electron microscopy studies. A plausible atomic model is proposed, which is constructed by two types of atomic clusters related to those in the Zn_7Mg_4 crystalline compound.

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1. Introduction

A quasicrystal is a solid with symmetries forbidden to ordinary crystals and without translational order. Its diffraction pattern composed of a set of delta function peaks is known to be explained by the projection method, by which the quasicrystal (quasi-lattice) is described with reference to a higher-dimensional analogue of a cubic lattice (Janssen, 1986). Meanwhile, the projection method predicts the possible occurrence of periodic crystals related to rational approximations of τ [$= (1 + 5^{1/2})/2$; golden ratio (Elser & Henley, 1985)]. The approximant crystals with a relatively large unit cell (typically in the order of a few Ångströms) have been generally found with the composition close to that of the corresponding quasicrystalline phases. In the case of two-dimensional quasicrystals, including decagonal phases, a τ -related inflation (or deflation) of lattice parameters occurs in the plane during the transformation between high-order and low-order approximant crystals (Zhang & Kuo, 1990).

In the Zn–Mg–RE (RE = rare-earth element or Y) systems, a thermodynamically stable decagonal (*d*) quasicrystal was discovered recently (Sato *et al.*, 1998), which should be classified as a Frank-Kasper type in the sense that atoms with different sizes are tetrahedrally packed (Frank & Kasper, 1958; Abe *et al.*, 1998); the other type is referred to as the Al-transition-metal (TM) group. A preliminary atomic structural model of the *d*-Zn–Mg–Dy phase was proposed based on the high-resolution transmission electron microscopy (HRTEM) study, with the aid of a local atomic configuration in the Zn_7Mg_4 crystalline compound (Abe *et al.*, 1999). During the study of the *d*-Zn–Mg–RE phase, we have discovered a trace of a novel crystalline phase with a large unit cell (Fig. 1) in the Zn–Mg–Dy alloy

in which the *d*-phase coexists. Here we propose a plausible atomic model of the phase based on electron diffraction and HRTEM (high-resolution transmission electron microscopy). The structure is shown to be constructed from two types of atomic clusters related to those in the Zn_7Mg_4 compound.

2. Experimental

The $\text{Zn}_{60}\text{Mg}_{38}\text{Dy}_2$ alloy was prepared by induction-melting pure Zn (99.9999%), Mg (99.99%) and Dy (99.9%) in a pyrolytic boron nitride crucible under an Ar atmosphere. Parts of the ingot were wrapped with Mo foil and sealed in Pyrex ampoules with Ar gas. They were annealed at 723 K for 50 h and subsequently at 673 K for 100 h. During this heat treatment, the $\text{Zn}_{60}\text{Mg}_{38}\text{Dy}_2$ phase with a Zn_7Mg_4 -type structure transforms into the *d*- $\text{Zn}_{58}\text{Mg}_{40}\text{Dy}_2$ phase (Sato *et al.*, 1998). For TEM observations, alloys were crushed and then dispersed on perforated carbon films. A Jeol 4000EX TEM with an accelerating voltage of 400 kV was used for the present study.

3. Results and discussion

Fig. 1(a) shows a selected area electron diffraction (SAED) pattern obtained from the $\text{Zn}_{60}\text{Mg}_{38}\text{Dy}_2$ alloy, taken with a selection aperture of 200 nm in diameter. The pattern cannot be indexed by any known phases in the Zn–Mg–Dy system so that the phase is novel and denoted as the τ -Zn–Mg–Dy phase. Only a few grains in the sample were found to exhibit the SAED pattern of Fig. 1(a) and the majority of the grains consist of *d*-Zn–Mg–Dy. We note that the τ -Zn–Mg–Dy phase appears during the transformation from the Zn_7Mg_4 crystal to the *d*-Zn–Mg–Dy quasicrystal, suggesting that τ -Zn–Mg–Dy is an intermediate phase during

the transformation. No significant chemical difference between the τ - and the d -phases was detected by energy-dispersive X-ray spectroscopy with TEM, so the composition of the τ -phase is approximately $\text{Zn}_{58}\text{Mg}_{40}\text{Dy}_2$ within an error of ± 3 at. %.

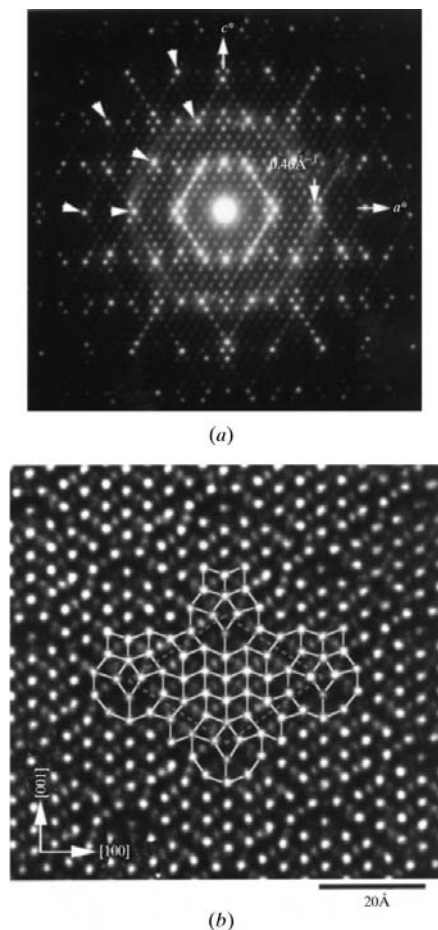


Figure 1
(a) Electron diffraction pattern of a novel phase τ -Zn-Mg-Dy formed in the $\text{Zn}_{60}\text{Mg}_{38}\text{Dy}_2$ alloy. (b) High-resolution image taken with the diffraction pattern of (a).

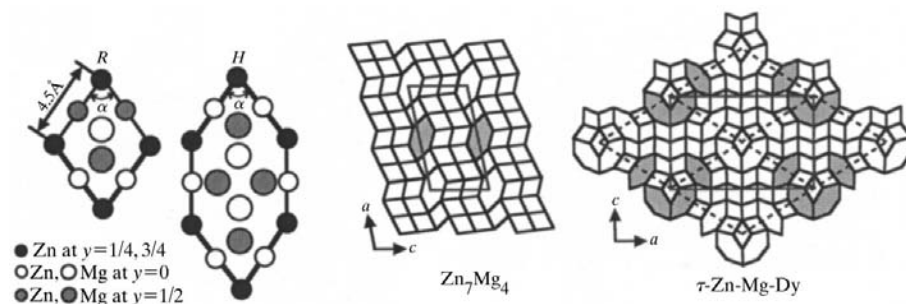


Figure 2
Schematic drawings of the atomic arrangement in the rhombus (R) and hexagon (H) tiles. Atomic structures of the Zn_7Mg_4 ($C2/m$, $a = 25.96$, $b = 5.24$, $c = 14.28$ Å, $\beta = 102.5^\circ$) and the τ -Zn-Mg-Dy phase are represented by R and H tile-clusters, in which unit cells are shown by gray lines. Note that the atomic positions shown in the R tile are representative; the positions are slightly shifted in each R tile in the Zn_7Mg_4 structure, in which α varies in the range $69.5\text{--}71.9^\circ$ (for the H tile, $\alpha = 71.55^\circ$).

Some of the τ -Zn-Mg-Dy phase coexisted with the d -Zn-Mg-Dy in one grain, where the incident beam direction of Fig. 1(a) was found to be parallel with the tenfold symmetry axis, indicating a pseudo-tenfold symmetry axis of τ -Zn-Mg-Dy. Although they are not at the perfect tenfold symmetry position, the ten intense reflections form a ring-like array around the transmitted spot, as exemplified by arrowheads in Fig. 1(a). Unfortunately, diffraction patterns from other zone axes could not be obtained for the τ -Zn-Mg-Dy phase, so that we cannot specify possible space groups at this stage. However, it can be assumed that a periodic length along the incident beam direction of Fig. 1(a) is the same as that of the d -phase, because of a reasonable orientation relationship between the phases. This will also be confirmed later by comparison with the Zn_7Mg_4 structure.

Fig. 1(b) shows a HRTEM image taken with the diffraction pattern of Fig. 1(a). The image was obtained from a relatively thicker part of the cleavage grain and taken with a larger defocus value than the Scherzer one (~ 45 nm for the present TEM). As demonstrated for d -Zn-Mg-Dy and the Zn_7Mg_4 structures, a center of icosahedral atomic column (distorted, see Fig. 3b in Abe *et al.*, 1998) is imaged as a bright dot under this imaging condition (Abe *et al.*, 1999), which is formed with 17 atoms and the structural unit of the phases. By connecting the bright dots with a distance of ~ 4.5 Å, it becomes clear that the structural basis can be interpreted as a two-dimensional arrangement of two types of tiles, as drawn in the figure: a rhombus (R) and a flattened-hexagon (H), subunits of the Penrose tiling. The basic atomic arrangement in these tiles can be derived from the Zn_7Mg_4 structure (Yarmoryuk *et al.*, 1975), as shown in Fig. 2, whose structure is also represented by these

tiles. On this basis, the τ -Zn-Mg-Dy phase can be interpreted as a two-dimensionally expanded structure of the Zn_7Mg_4 phase in the sense that the both structures are constructed by the same atomic clusters with a definite b length. Note that Zn atoms always lie on the edges, while the Mg atoms are placed at the interior of the tiles, representing a chemically ordered state of the structure. An important feature in connecting these atomic cluster tiles is that, for the case of R and H shown in Fig. 2, only the bold edges of R can be coincident with those of H due to the Zn level $y = 0$. This results in the appearance of H shifted by $1/2$ along the b axis with respect to the other H atoms after tiling, which is shown in gray in Fig. 2, emerging out a rectangular unit cell. Thus, the τ -phase has an orthorhombic cell with $a = 39.2$, $b = 5.1$ and $c = 25.0$ Å, and a plausible atomic arrangement is constructed by R and H tile-clusters. A stoichiometry of the τ -phase is estimated to be $\text{Zn}_{62.3}\text{Mg}_{37.7}$ by assuming a perfectly ordered structure (neither occupational nor chemical disorder for all atomic sites), which is approximately in good agreement with the observed composition of $\text{Zn}_{58}\text{Mg}_{40}\text{Dy}_2$ (Dy could substitute the Mg site in terms of atomic size). A kinematical electron diffraction pattern calculated for the present τ -Zn-Mg-Dy structural model, shown in Fig. 3, reproduces well the observed intensity distribution, especially for the strong reflections (some discrepancies for the weak reflections could be attributed to a multiple-scattering effect in electron diffraction). This confirms that the basic atomic arrangement in the present τ -Zn-Mg-Dy structural model is valid enough.

We note that the observed lattice parameters of the τ -Zn-Mg-Dy are fairly well reproduced by its tiling feature (Fig. 2) with an ideal α value of 72° for each tile ($a = 39.50$, $c = 25.28$ Å), indicating a considerably small distortion from the ideal tiles in the Penrose tiling. According to the definition of rational approximants, the present orthorhombic phase might be regarded as an $8/5\text{--}5/3$ approximant crystal of the d -Zn-Mg-Dy phase, predicting $a = 40.7$ and $c = 21.4$ Å when the corresponding edge length of Penrose rhombus a_R is assumed as 4.3 Å from the diffraction pattern of the d -Zn-Mg-Dy quasicrystal (Abe *et al.*, 1998). However, discrepancies between predicted and observed unit-cell parameters are relatively large (especially for c) as compared with some of the orthorhombic approximant crystals in Al-TM alloys (Zhang & Kuo, 1990), so that τ -Zn-Mg-Dy cannot be well identified as the approximant crystal. In fact,

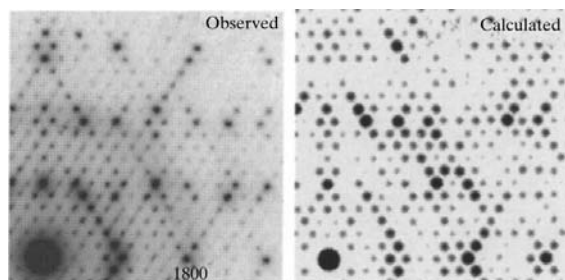


Figure 3
Observed and calculated electron diffraction intensity distributions for the τ -Zn-Mg-Dy phase. The observed intensity is shown by inverse contrast to that in Fig. 1.

an interval between the transmitted and the strong spot (18 0 0) is divided into nine parts by weak spots, which is not expected from a Fibonacci sequence (1, 2, 3, 5, 8,...). It is interesting to note that a progression 1, 4, 5, 9,... derived by dropping 2 and 3 in a Fibonacci sequence explains the appearance of relatively strong $h00$ reflections.

In the well identified Al-TM approximant crystals, atomic clusters with decagonal symmetry are connected by linkages, and the corresponding quasicrystals are shown to be formed by quasiperiodic arrangement of these atomic clusters with the same local

connection (Hiraga, 1998). This is responsible for the nearly perfect tenfold symmetric appearance of the ten intense reflections in the well identified Al-TM approximant crystals. As discussed in the previous paper, such an arrangement of symmetric decagonal clusters cannot be defined both in the Zn_7Mg_4 crystal and the d -Zn-Mg-Dy quasicrystal (Abe *et al.*, 1999), which is also consistent with the structural characteristic of τ -Zn-Mg-Dy; its structure can be interpreted by the R and H tiles (Fig. 2), at whose vertices the distorted icosahedral atomic columns (Abe *et al.*, 1998) are placed, resulting in the distorted-decagon appearance of ten intense reflections (Fig. 1). This supports an idea that the d -Zn-Mg-Dy quasicrystal structure can be explained by a simple atomic decoration of the Penrose tiling (Abe *et al.*, 1999), not by the atomic clusters with decagonal symmetry which have been used for the structural description of d -Al-TM quasicrystals. Further details on the structure of

the d -Zn-Mg-Dy phase in terms of the R and H tile-clusters will be discussed elsewhere.

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