The intermetallic compound Mg$_{21}$Zn$_{25}$

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Received 23 July 2002
Accepted 2 October 2002
Online 22 October 2002

The crystal structure of the intermetallic compound henicosa-magnesium pentacosazinc, Mg$_{21}$Zn$_{25}$, has been determined by single-crystal X-ray diffraction. It is isomorphous with Zr$_{21}$Re$_{25}$ and deviates slightly from the rules that define the Frank–Kasper phases.

Comment

The intermetallic phase with a composition close to MgZn has been reported several times in the literature [Tarschisch, 1933; Clark & Rhines, 1957; Clark et al., 1988; Khan, 1989; International Centre for Diffraction Data (ICDD), card 08-0206 (ICDD, 2001)], and its composition was reported as Zn-rich. The crystal structure of stoichiometric MgZn (P6$_3$/mmc, $a = 10.66$ and $c = 17.16$ Å) was given by Tarschisch (1933). It is derived from the hexagonal structure of the Frank–Kasper (Frank & Kasper, 1958, 1959) phase of MgZn$_2$ (Friauf, 1927) by a substitution of one Zn site by Mg and deformation of the coordination icosahedra. It was recognized later (McKeehan, 1935) that the structure has orthorhombic symmetry (Imm$_2$, $a = 5.33$, $b = 17.16$ and $c = 9.23$ Å). However, short interatomic Mg–Zn distances of 2.23 Å were present in the structural model.

The phase reported by Khan (1989) has the nominal composition MgZn and its powder pattern was indexed with a hexagonal lattice ($a = 25.69$ and $c = 18.104$ Å), showing systematic extinctions corresponding to an R-centred cell. Another, very similar, powder pattern of a compound with the nominal composition MgZn was also reported, in the PDF-2 database (ICDD, 2001). The compound Mg$_{21}$Zn$_{25}$ presented here is isomorphous with Zr$_{21}$Re$_{25}$ (Cenzual et al., 1986). It deviates slightly from the rules that define the Frank–Kasper phases and does not precisely follow the equations given by Shoemaker & Shoemaker (1986) that account for the numbers of each Frank–Kasper coordination polyhedron in the structure. Atom Mg2 is coordinated by Mg$_4$Zn$_{12}$, atom Mg1 by Mg$_7$Zn$_7$, atom Mg3 by Mg$_5$Zn$_6$ and atom Mg4 by Mg$_{10}$Zn$_4$. Atoms Zn4 and Zn6 are coordinated by Mg$_6$Zn$_6$, atoms Zn1, Zn2 and Zn3 by Mg$_7$Zn$_5$, and atom Zn5 by Mg$_8$Zn$_4$. The Zn—Zn, Zn—Mg and Mg—Mg distances are in the ranges 2.57–2.72, 2.95–3.18 and 3.01–4.03 Å, respectively. The crystal structure of Mg$_{21}$Zn$_{25}$ can be constructed from (00l) slabs (Fig. 1) that are repeated three times in the unit cell by R-centring.

In Cenzual et al. (1986), the coordination of Zr4 (here Mg4) was described as a Zr$_8$Re$_4$ icosahedron. If two additional Mg atoms at distances of 4.032 Å from Mg4 are added to the Mg4 coordination icosahedron, we get an Mg$_{10}$Zn$_4$ coordination polyhedron, which is not of the Frank–Kasper type. However, we prefer this description because it fills all the available space in the structure (Fig. 1).

The calculated powder pattern of Mg$_{21}$Zn$_{25}$ agrees better with that reported in the PDF-2 database (ICDD, 2001) than with that reported by Khan (1989). The cell parameters reported by Khan do not agree exactly with ours. The $a$ parameter can be considered to be essentially the same as our value (no experimental errors are given by Khan). However, half the $c$ parameter reported by Khan is significantly different from our value for the $c$ parameter. No doubling of the $c$ length was observed in our data. It is necessary to note that the experiment carried out by Khan was performed on rapidly cooled ribbons that were then annealed at low temperature (450 K); therefore, intermediate phases that were not in equilibrium cannot be excluded.

Experimental

A sample of nominal composition MgZn was melted by placing a compressed mixture of Mg powder (Strem Chemical, 99.8%) and Zn powder (Fluka, p.a. 99.0%) into a quartz ampoule, which was sealed under an argon pressure of 0.3 bar (1 bar = 10$^5$ Pa) and annealed at 573 K for 1 d. The ingot (1 g) was crushed into several pieces and powdered under a protective argon atmosphere. In spite of melting losses of about 2.3 wt%, the X-ray powder pattern indicated the
presence of mainly Mg_{21}Zn_{25}, with small amounts of Mg_{51}Zn_{20} and Mg_{88}Zn_{12} as minor impurities. Several single crystals of suitable size for X-ray analysis were found in the crushed sample and were examined by the Laue method.

Crystal data

Mg_{21}Zn_{25}
M_r = 2144.72
Trigonal, R3c
a = 25.7758 (13) Å
b = 8.7624 (6) Å
V = 5041.7 (5) Å³
Z = 6
D_x = 4.238 Mg m⁻³

Mo Kα radiation
Cell parameters from 2000 reflections
θ = 3–25°
μ = 17.85 mm⁻¹
T = 293 K

Irregular, metallic dark grey
0.09 × 0.07 × 0.04 mm

Data collection

Stoe IPDS diffractometer
φ oscillation scans
Absorption correction: analytical
(X-RED in IPDS; Stoe & Cie, 1999)
T = 293 K

Cell parameters from 2000 reflections
θ = 3–25°
k = −31 → 31
l = −10 → 10
200 standard reflections
frequency: 10 min
intensity decay: none

Three non-coherent domains with Mg_{21}Zn_{25} cell parameters were identified in the crystal. The domain reflections were separated in the process of image integration. From 12 063 measured reflections of the first domain, 2274 reflections were rejected because of overlap with reflections of the second and third domains; the mean F²/σ(F²) value was 7.9. In the second domain, 12 090 reflections were measured and the mean F²/σ(F²) value was 4.0. In the third domain, 12 064 reflections were measured and the mean F²/σ(F²) value was 3.1. Only the data of the first domain were used for the structure solution and refinement. The R factor statistics show no systematic deviation of different reflection groups from the mean, whether dependent on hkl, F_obs or sin(θ)/λ.

Data collection: EXPOSE in IPDS (Stoe & Cie, 1999); cell refinement: CELL in IPDS; data reduction: TWIN and X-RED in IPDS; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ATOMS (Dowty, 1993); software used to prepare material for publication: WinGX (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ1025). Services for accessing these data are described at the back of the journal.

References