Acta Crystallographica Section C
Crystal Structure
Communications
ISSN 0108-2701

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 henicosamagnesium 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 ($Imm2$, 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_4Zn_{12}, atom Mg1 by Mg_7Zn_7, atom Mg3 by Mg_7Zn_8 and atom Mg4 by $Mg_{10}Zn_4$. Atoms Zn4 and Zn6 are coordinated by Mg_6Zn_6, atoms Zn1, Zn2 and Zn3 by Mg_7Zn_5, and atom Zn5 by Mg_8Zn_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.

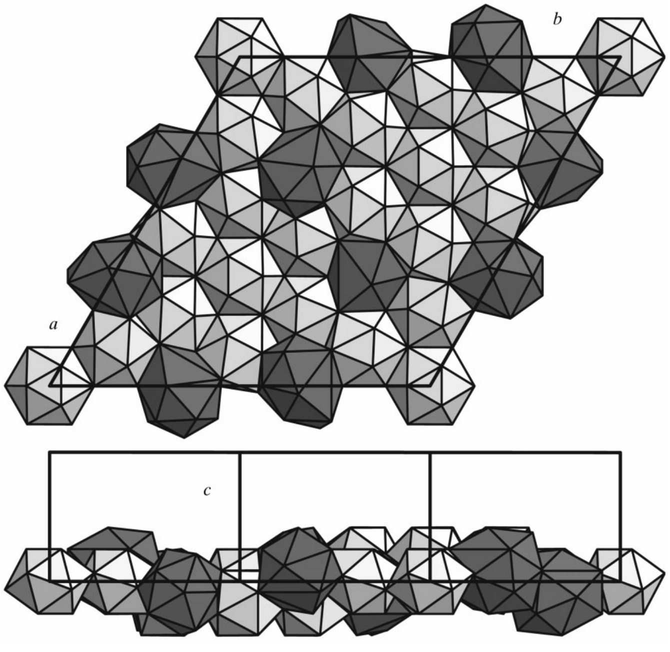

Figure 1
One structural slab (00l) of $Mg_{21}Zn_{25}$ at $z \sim 0$, composed of the Zn6Mg_6Zn_6 and Zn3Mg_7Zn_5 icosahedra (light grey) and the Mg4$Mg_{10}Zn_4$ polyhedron (dark grey).

In Cenzual *et al.* (1986), the coordination of Zr4 (here Mg4) was described as a Zr_8Re_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

DOI: 10.1107/S0108270102018103

presence of mainly $Mg_{21}Zn_{25}$, with small amounts of $Mg_{51}Zn_{20}$ and $MgZn_2$ 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, $R\bar{3}c$
$a = 25.7758\ (13)$ Å
$c = 8.7624\ (6)$ Å
$V = 5041.7\ (5)$ Å^3
$Z = 6$
$D_x = 4.238$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 2000 reflections
$\theta = 3$–$25°$
$\mu = 17.85$ mm^{-1}
$T = 293$ K
Irregular, metallic dark grey
$0.09 \times 0.07 \times 0.04$ mm

Data collection

Stoe IPDS diffractometer
φ oscillation scans
Absorption correction: analytical (*X-RED* in *IPDS*; Stoe & Cie, 1999)
$T_{\min} = 0.363$, $T_{\max} = 0.455$
9789 measured reflections
1097 independent reflections
780 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.087$
$\theta_{\max} = 25.9°$
$h = -31 \rightarrow 31$
$k = -31 \rightarrow 30$
$l = -10 \rightarrow 10$
200 standard reflections
frequency: 10 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.032$
$wR(F^2) = 0.076$
$S = 0.96$
1097 reflections
73 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0371P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.78$ e Å^{-3}
$\Delta\rho_{\min} = -1.63$ e Å^{-3}

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 $F^2/\sigma(F^2)$ value was 7.9. In the second domain, 12 090 reflections were measured and the mean $F^2/\sigma(F^2)$ value was 4.0. In the third domain, 12 064 reflections were measured and the mean $F^2/\sigma(F^2)$ 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, $F_{\rm obs}$ or $\sin(\theta)/\lambda$.

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: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (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.

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