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$Ce_{20}Mg_{19}Zn_{81}$: a new structure type with a giant cubic cell

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Icosacerium nonadecamagnesium henoctacontazinc, $Ce_{20}Mg_{19}Zn_{81}$, synthesized by fritting of the pure elements with subsequent arc melting, crystallizes with an unusually large cubic unit cell [space group $F\bar{4}3m$, a = 21.1979 (8) Å] and represents a new structure type among the technologically important family of ternary rare earth–transition metal–magnesium intermetallics. The majority of atoms (two Ce and five Zn) display $.3m$ site symmetry, two Ce and one Mg atom occupy three $2.mm$ positions, one Mg and one Zn have $\bar{4}3m$ site symmetry, one Mg and three Zn atoms sit in $..m$ positions, and one Zn atom is in a general position. The $Ce_{20}Mg_{19}Zn_{81}$ structure can be described using the geometric concept of nested polyhedral units, by which it consists of four different polyhedral units, *viz.* *A* ($Zn+Zn_4+Zn_4+Zn_{12}+Ce_6$), *B* ($Mg+Zn_{12}+Ce_4+Zn_{24}+Ce_4$), *C* ($Zn_4+Zn_{12}+Mg_6$) and *D* ($Zn_4+Zn_4+Mg_{12}+Ce_6$), with the outer construction unit being an octahedron or tetrahedron. All interatomic distances in the structure indicate metallic-type bonding.

Comment

Ternary compounds containing a rare earth (RE), a transition metal (M) and magnesium represent a growing class of materials which attract attention due to their physical properties and applications as modern lightweight alloys and hydrogen storage materials. The crystal structures, physical properties and hydrogenation behaviour of these materials have been reviewed (Rodewald *et al.*, 2007). The appearance of numerous quasicrystals has also been observed in these systems (Steurer & Deloudi, 2008). The Ce–Mg–Zn ternary system was first reported by Melnyk *et al.* (1978). The isothermal section of the phase diagram was partially constructed up to 60 at.% of Zn and 50 at.% of Ce at 573 K. Four new ternary compounds with preliminary compositions $\sim CeMg_7Zn_{12}$, $\sim Ce(Mg_{0.5–0.85}Zn_{0.5–0.15})_9$, $\sim CeMg_3Zn_5$ and $Ce_2Mg_3Zn_3$ were reported in this region. The last compound was found to crystallize with a cubic unit cell (a = 7.064 Å), whereas the crystal structures of the first three compounds remain unknown. We decided to explore the rest of the phase diagram starting from the Zn-rich corner.

The most transition metal-rich phases known in the literature so far are $REMg_2M_9$ and $REMgM_4$. The first series adopts either a rhombohedral $PuNi_3$ type (space group $R\bar{3}m$; Kadir *et al.*, 1997) or a hexagonal $TbCu_9Mg_2$ type (space group $P6_3/mmc$) structure (Solokha *et al.*, 2006). The second series crystallizes with the cubic $MgCu_4Sn$ structure type (space group $F\bar{3}m$), an ordered version of the Laves phase related structure $AuBe_5$ (Kadir *et al.*, 2002; Sarrao *et al.*, 1999). Many of these $REMgM_4$ alloys have been studied intensively for hydrogen storage purposes (Wang, Zhou, Cheng *et al.*, 2004; Xu *et al.*, 2005). They show excellent discharge capacities of the order of 400 mA h g^{-1} and can keep their discharge stability over 50 cycles. The influence of different factors (*e.g.* mechanical alloying, or rare earth or transition metal substitution) on the discharge characteristics of these alloys has also been investigated (Wang, Zhou, Gu *et al.*, 2004; Zhang *et al.*, 2005; Li *et al.*, 2005). We present here the results of a crystallographic study of a new transition metal-rich compound, *viz.* $Ce_{20}Mg_{19}Zn_{81}$.

The crystal structure of this compound is fairly complicated, with a cubic unit cell containing 480 atoms. The projection of the unit cell of $Ce_{20}Mg_{19}Zn_{81}$ and the coordination polyhedra of the atoms are shown in Fig. 1. The number of neighbour atoms correlates well with the sizes of the central atoms. The largest Ce atoms are enclosed in 16-, 17- and 18-vertex polyhedra. Mg atoms are characterized by Frank–Kasper or pseudo-Frank–Kasper polyhedra, having coordination number (CN) 15 or 16. Atom Zn1 is surrounded by 14 neighbours in the form of a distorted rhombododecahedron (CN 14). The remaining Zn atoms (Zn2–Zn10) have icosahedral symmetry with CN 10–13. The shortest interatomic distances (Table 1) are in the ranges typical for intermetallic

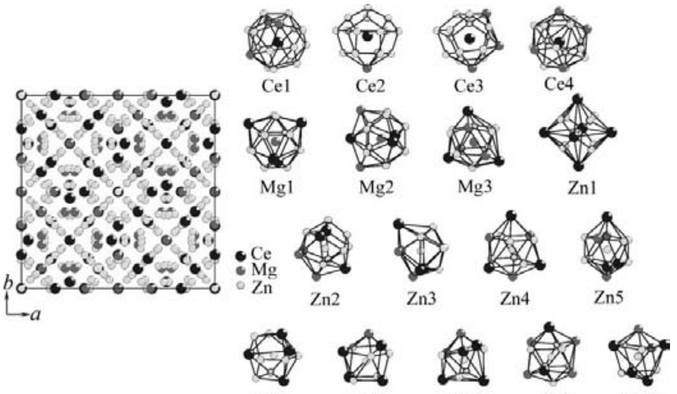

Figure 1
A projection of the $Ce_{20}Mg_{19}Zn_{81}$ unit cell and the coordination polyhedra of the atoms. Ce, Mg and Zn atoms are drawn as black, dark-grey and light-grey circles, respectively.

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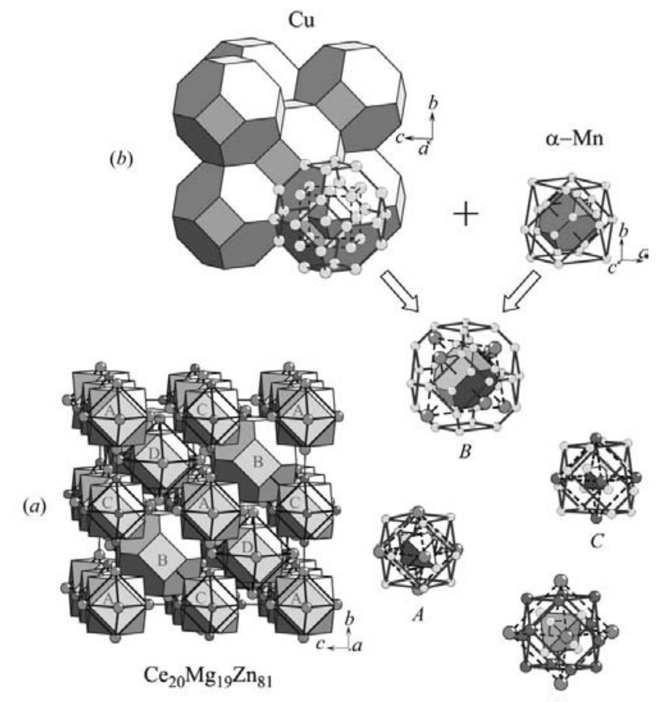

Figure 2
(*a*) The nested polyhedral units as construction elements of $Ce_{20}Mg_{19}Zn_{81}$. (*b*) The *B* unit as a 'hybrid' of α-Mn and fcc Cu structural fragments.

compounds of these elements and indicate metallic-type bonding. The structure can be assigned to the class No. 5 (CN 12 for the smallest atom; icosahedron as the coordination polyhedron), according to the classification scheme of Krypyakevich (1977).

Chabot *et al.* (1981) proposed the geometric concept of nested polyhedral units for the description of complicated cubic structures. According to this concept, seven different polyhedral units were proposed as basic units, with the outermost polyhedron always being a cubo-octahedron. With respect to the spatial arrangement of nested polyhedral units, cubic structures were divided into two groups with isolated and linked units, respectively. The crystal structure of $Ce_{20}Mg_{19}Zn_{81}$ can also be described by means of isolated polyhedral units, although the construction units here are different from those proposed earlier. We can distinguish four different units, *A*, *B*, *C* and *D* (Fig. 2*a*). Unit *A* (27 atoms) consists of a central atom (C) surrounded by a small inner tetrahedron (IT) and a larger outer tetrahedron (OT). Further away from the centre are a cubo-octahedron (CO) and an octahedron (OH). The *B* unit (45 atoms) includes the following elements: C–TT–IT–TCO–OT. As the construction elements of the *B* nested unit, a truncated tetrahedron (TT) and a truncated cubo-octahedron (TCO) also occur. The *C* unit (22 atoms) includes T–CO–OH, and the *D* unit (26 atoms) is characterized by an IT–OT–CO–OH sequence.

If we compare the *A* and *D* units we can see that they are almost the same and only differ by one atom, which centres the *A* unit. Both these units correspond to the γ-brass basic unit with or without a central atom. Unit *C* is related to the Ti_2Ni structure type with a slightly different sequence of geometric forms. The *B* unit cannot be fully described by the Chabot concept. Instead, we can apply here the ideas of Bodak *et al.* (2006), who proposed the description of complicated cubic structures starting from four 'arystotypes', namely diamond, Cu, CsCl and W, from the example of cubic rare earth-containing compounds. On this basis, we can assume that the *B* unit is a 'hybrid' of α-Mn and face-centred cubic (fcc) Cu units in which the internal part (C–TT–IT) is the same as in α-Mn and the external part (TCO) is identical to that in fcc Cu (Fig. 2*b*). The number of atoms in the unit cell is equal to the sum of the atoms in each unit: (4 × 27) + (4 × 22) + (4 × 26) + (4 × 45) = 480 (Pearson code cF480). Taking the nested polyhedral units as 'pseudo-atoms', we can also consider $Ce_{20}Mg_{19}Zn_{81}$ to belong to the LiMgPdSn structure type ($F\bar{4}3m$, cF16).

Experimental

To avoid loss of magnesium and zinc due to their vapour pressure at higher temperatures, the alloys were prepared in two steps. First, powders of the pure metals with a Ce:Mg:Zn stoichiometry of 1:1:4 were pressed into a pellet, enclosed in an evacuated silica ampoule (internal pressure 10^{-5}–10^{-6} Pa) and placed in a resistance furnace with a thermocouple controller. The heating process was carried out in a consecutive order, increasing the temperature from 673 to 1073 K over a period of 6 d. The alloy was then annealed at this temperature for 4 h and cooled slowly to room temperature. In the second step, the pellet was remelted in an arc furnace under an argon atmosphere at least three times in order to ensure homogeneity. The total weight loss after the melting procedures was less than 2 wt.%. The brittle sample was stable in air, showing a metallic lustre. Wavelength-dispersive spectrometry and electron probe microanalysis (CAMECA SX100 analyser) were used to control the number of phases and their content in the sample. Various point analyses on this phase were in good agreement with the ideal composition determined by the single-crystal X-ray data (an average result is 17.6 at.% Ce, 14.7 at.% Mg and 67.7 at.% Zn). Irregularly shaped single crystals, exhibiting a metallic lustre, were isolated by mechanical fragmentation from the alloys.

Crystal data

$Ce_{20}Mg_{19}Zn_{81}$
$M_r = 8559.26$
Cubic, $F\bar{4}3m$
$a = 21.1979$ (8) Å
$V = 9525.3$ (6) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 29.39$ mm^{-1}
$T = 295$ (2) K
0.11 × 0.09 × 0.07 mm

Data collection

Oxford Diffraction Xcalibur diffractometer
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2005)
$T_{\min} = 0.056$, $T_{\max} = 0.122$
1009 measured reflections
544 independent reflections
388 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.034$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.101$
$S = 1.01$
544 reflections
73 parameters
$\Delta\rho_{\max} = 1.63$ e Å^{-3}
$\Delta\rho_{\min} = -1.89$ e Å^{-3}
Absolute structure: Flack (1983), with 465 Friedel pairs
Flack parameter: 0.3 (2)

Table 1
Selected bond lengths (Å).

Ce2—Zn6	3.044 (9)	Mg3—Ce3^{ii}	3.325 (13)
Mg2—Zn10^{i}	3.024 (8)	Zn1—Zn6	2.598 (8)

Symmetry codes: (i) *z*, *x*, *y*; (ii) −*y*, *z*, −*x*.

The systematic absences indicated five possible space groups, $Fm\overline{3}$ (No. 202), *F*23 (No. 196), $F\overline{4}3m$ (No. 216), $Fm\overline{3}m$ (No. 225) and *F*432 (No. 209). The statistical test of the distribution of the *E* values (Farrugia, 1999) suggested that the structure is noncentrosymmetric with a probability of 73.49%. The structure solution and refinement clearly indicated that $Ce_{20}Mg_{19}Zn_{81}$ crystallizes in the noncentrosymmetric space group $F\overline{4}3m$. The occupancy parameters were refined in separate series of least-squares cycles. No significant deviations were found and in the final cycles the ideal values were assumed again. After that, the data were refined with anisotropic displacement parameters for all atoms. The atomic coordinates were standardized using the *STRUCTURETIDY* program (Gelato & Parthé, 1987). The final difference Fourier syntheses revealed no significant residual peaks: the highest maximum residual electron density was 1.62 e Å^{-3} from atom Zn3 and the deepest hole was −1.89 e Å^{-3} from Zn1.

Data collection/cell refinement: *CrysAlis CCD* (Oxford Diffraction, 2004); data reduction: *CrysAlis RED* (Oxford Diffraction, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3145). Services for accessing these data are described at the back of the journal.

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