The Crystal Structure of $GdZn_3$

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The crystal structure of $GdZn_3$ was refined using single-crystal X-ray diffraction data: YZn_3 type, space group *Pnma*, $Z = 4$, $a = 6.7250(13)$, $b = 4.4620(9)$, $c = 10.201(2)$ Å, $R_1 = 0.049$, $wR_2 = 0.082$, 303 F^2 values, 25 variables. The zinc atoms build up a three-dimensional network with short Zn–Zn distances, while the Gd atoms are well separated from each other. The coordination number is 17 for Gd, and 10 and 12 for the Zn atoms.

Key words: Intermetallics, Gadolinium, Zinc, Crystal Chemistry

Introduction

The binary system Gd-Zn is rich in intermetallic phases, especially in the region with high content of Zn [1, 2]. Ten binary compounds (with the structure types (ST) in parentheses) with the compositions: GdZn (ST CsCl) [3], $GdZn_2$ (ST $CeCu_2$) [4], $GdZn_3$ (ST YZn_3) [1, 2, 5], Gd_3Zn_{11} (ST La_3Al_{11}) [1, 2], $Gd_{13}Zn_{58}$ (ST $Gd_{13}Zn_{58}$) [1, 2, 6 – 8], Gd_3Zn_{22} (ST Gd_3Zn_{22}) [1, 2], Gd_2Zn_{17} (ST Th_2Zn_{17} or Th_2Ni_{17}) [1, 2, 9, 10], and $GdZn_{12}$ (ST $ThMn_{12}$) [1, 2, 10] have been reported. They have mostly been characterized thermodynamically as part of temperature-composition diagram constructions [2]. However, the majority of the phases are not well investigated and characterized crystallographically. A good example is $Gd_{13}Zn_{58}$, previously known as "Gd_2Zn_9" [7], which crystallizes in its own structure type (hexagonal system, space group $P6_3/mmc$). Its crystal structure was first determined in 1971 [7]. The recent investigation [8] revealed that $Gd_{13}Zn_{\sim 58}$ is a complex quasicrystal approximant which, in fact, crystallizes in space group $P6_3mc$ and features partial occupancy of some atom sites and, consequently, some flexibility in composition. Another interesting compound is Gd_2Zn_{17} which has two polymorphic modifications with the Th_2Zn_{17} [9] and Th_2Ni_{17} [10] structure types, characterized by partial disorder with a description by split positions. The structure modification can be achieved either by temperature treatment, a slight shift in composition or small admixtures of a third component. The existence of a binary compound $GdZn_3$ was reported, and it was stated that it adopts the YZn_3 structure type [1, 2, 5], however, only cell constants have been refined by means of powder X-ray diffraction, and no structure determination was performed. Moreover, it was found that $CeZn_3$ has a slightly different structure with space group *Cmcm* [1]. In this paper we report on the single-crystal structure investigation of binary $GdZn_3$.

Experimental

$GdZn_3$ was obtained in the ternary samples with compositions $Gd_{30}Zn_{65}In_5$ and $Gd_{25}Zn_{70}In_5$ during a systematic study of the Gd-Zn-In system. The starting materials for the preparation of the Gd-Zn-In samples were ingots of gadolinium, zinc and indium, all with stated purities better than 99.95 wt.-%. The mixture of the elements was placed in a corundum crucible and sealed in a quartz tube under high vacuum (better than 10^{-5} mbar). The samples were heated to 1070 K, held at this temperature for 1 h and subsequently cooled to the annealing temperature of 870 K during 83 h. Subsequently, the annealing was carried out for 14 d. After that thermal treatment the ampoules were cooled to room temperature by switching off the furnace. The obtained ingots were polycrystalline specimens with metallic luster, stable in air over months.

Powder X-ray diffraction data were collected on an automatic diffractometer Bruker D8 advance. Phase analysis was performed using the program POWDERCELL [11], and refinement of the cell parameters was achieved with the program FULLPROF [12, 13]. In accordance with the phase analysis, two samples with compositions $Gd_{25}Zn_{70}In_5$ and $Gd_{30}Zn_{65}In_5$ contained the phase which was indexed on the basis of previously reported $GdZn_3$ with the YZn_3 structure type. This compound exists in equilibrium with the solid solution of In in $GdZn_2$ (KHg_2 structure type) [4]. The cell parameters of $GdZn_3$, refined for both samples, had close values with a cell volume of 305.7 $Å^3$, which is in good correlation with the single-crystal data.

The single crystal was extracted from the sample with the composition $Gd_{30}Zn_{65}In_5$. Intensity data were collected on a Stoe IPDS-II diffractometer with MoK_α radiation ($\lambda =$

Table 1. Crystal data and structure refinement for $GdZn_3$.

Molar mass, g mol^{-1}	353.36
Crystal system	orthorhombic
Space group; Z	*Pnma*; 4
Cell parameters	
a, Å	6.7250(13)
b, Å	4.4620(9)
c, Å	10.201(2)
Cell volume V, Å^3	306.12(10)
Calculated density, g cm^{-3}	7.67
Absorption coefficient, mm^{-1}	44.3
$F(000)$, e	616
θ range, deg	3.6–25
Range in *hkl*	$0 \le h \le 7$; $-5 \le k \le 5$; $-12 \le l \le 0$
Measured reflections	499
Independent reflections/R_{int}	303/0.048
Reflections with $I > 2\,\sigma(I)/R_\sigma$	214/0.086
Data/refined parameters	303/25
Goodness-of-fit on F^2	0.997
R_1 [$F^2 > 2\,\sigma(F^2)$]	0.049
wR_2 (F^2)	0.082
Largest diff. peak/hole, e Å^{-3}	1.49/−3.10

0.71073 Å). Scans were taken in the $\omega/2\theta$ mode. A numerical absorption correction was applied to the data set. Analyses of the systematic extinctions led to the possible space groups *Pnma* and $Pna2_1$. The space group with the higher symmetry, *Pnma*, was found to be correct during the structure refinement. The starting atomic parameters were deduced from an automatic interpretation of Direct Methods, and the structure was successfully refined using full-matrix least-squares on F^2 with anisotropic atomic displacement parameters for all atoms using the program SHELXL-97 [14, 15]. Some details of the data collection and refinement parameters are given in Table 1. As the sample contained small amounts of indium, all atomic sites were checked for mixed Zn/In or Gd/In occupancy. However, the refinement resulted in full occupancy exclusively by Zn or Gd atoms in the corresponding crystallographic positions. Final difference Fourier syntheses revealed no significant residual peaks. The largest residual densities were close to the gadolinium sites and most likely resulted from absorption effects. The final atomic coordinates and equivalent isotropic displacement parameters are given in Table 2. The anisotropic displacement parameters of all atoms are listed in Table 3.

Table 2. Atomic coordinates and isotropic displacement parameters (Å^2) of $GdZn_3$.

Atom	Wyck.	x	y	z	U_{eq}
Gd	4*c*	0.2754(3)	$^1/_4$	0.34074(16)	0.0186(4)
Zn1	4*c*	0.2248(6)	$^1/_4$	0.0451(4)	0.0206(8)
Zn2	4*c*	0.4209(6)	$^1/_4$	0.6448(4)	0.0205(9)
Zn3	4*c*	0.0398(5)	$^1/_4$	0.6082(4)	0.0230(10)

Table 3. Anisotropic displacement parameters (Å^2) of $GdZn_3$.

Atom	U_{11}	U_{22}	U_{33}	U_{13}
Gd	0.0164(8)	0.0165(8)	0.0230(7)	−0.0023(9)
Zn1	0.0211(19)	0.0194(19)	0.0213(16)	0.0051(18)
Zn2	0.0229(19)	0.017(2)	0.0219(19)	−0.0052(19)
Zn3	0.017(2)	0.027(2)	0.0250(18)	0.0049(19)

$U_{12} = U_{23} = 0$.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the deposition number CSD-426414.

Results and Discussion

$GdZn_3$ belongs to the YZn_3 structure type with one 4*c* Wyckoff site occupied by Gd and three others by Zn atoms. A projection of the unit cell on the *xz* plane and coordination polyhedra of the atoms are shown in Figs. 1 and 2, respectively.

Interatomic distances are in good correlation with the respective sum of the atomic radii [16] (Table 4). Similar to YZn_3 and $HoZn_3$ [5], strong bonding is observed between the Zn atoms with a maximum distance reduction of −2.78 % in comparison with the sum of

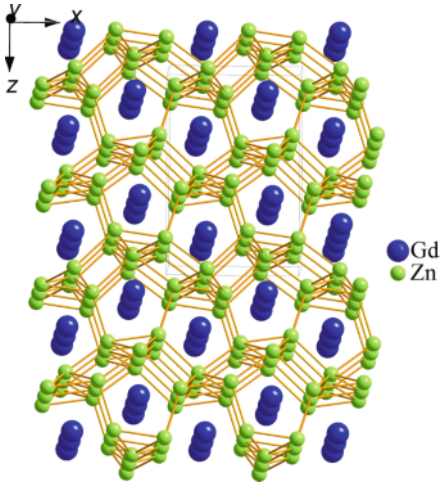

Fig. 1 (color online). The crystal structure of $GdZn_3$. The three-dimensional Zn network is emphasized.

Atom		d (Å)	Δ (%)	CN	Atom		d (Å)	Δ (%)	CN
Gd1	2Zn2	3.028(3)	−3.37	17	Zn2	1Zn3	2.590(5)	−2.78	10
	1Zn1	3.035(4)	−3.16			2Zn1	2.640(3)	−0.89	
	2Zn1	3.053(3)	−2.57			1Zn3	2.644(6)	−0.77	
	2Zn3	3.121(3)	−0.41			1Zn1	2.816(6)	5.70	
	1Zn3	3.155(4)	0.67			2Gd	3.028(3)	−3.37	
	1Zn1	3.239(5)	3.34			1Gd	3.252(4)	3.78	
	1Zn2	3.252(4)	3.78			2Gd	3.273(3)	4.45	
	2Zn2	3.273(3)	4.45		Zn3	1Zn2	2.590(5)	−2.78	12
	2Zn3	3.486(3)	11.22			1Zn1	2.633(6)	−1.16	
	2Gd	3.838(3)	6.50			1Zn2	2.644(6)	−0.77	
	1Zn1	3.882(5)	23.85			2Zn1	2.810(3)	5.49	
Zn1	1Zn3	2.633(6)	−1.16	10		2Gd	3.121(3)	−0.41	
	2Zn2	2.640(3)	−0.89			1Gd	3.155(4)	0.67	
	2Zn3	2.810(3)	5.49			2Zn3	3.184(4)	19.52	
	1Zn2	2.816(6)	5.70			2Gd	3.486(3)	11.22	
	1Gd	3.035(4)	−3.16						
	2Gd	3.053(3)	−2.57						
	1Gd	3.239(5)	3.34						

Table 4. Interatomic distances (d, Å), Δ values ($\Delta = 100(d - \Sigma r)/\Sigma r$, where Σr is the sum of the respective atomic radii) and coordination numbers of the atoms in $GdZn_3$.

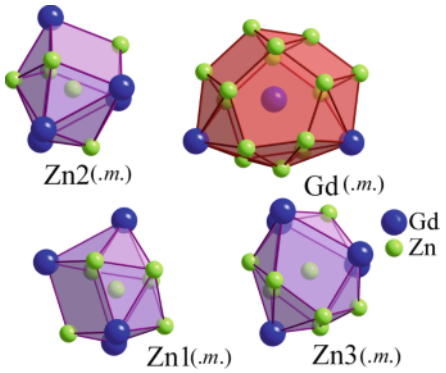

Fig. 2 (color online). The coordination polyhedra of the atoms in $GdZn_3$.

the atomic radii [16]. Thus, Zn atoms are bonded to each other and form a 3D network (Fig. 1). Each Zn2 and Zn3 is connected to five other Zn atoms at distances of 2.590(5) – 2.816(6) Å. The Zn1 atom has direct bonds to six Zn atoms with distances ranging from 2.633(6) to 2.816(6) Å.

The gadolinium atoms fill large cages within the Zn network (Fig. 2). They are bound to the network *via* Gd–Zn contacts (minimum distance is 3.028(3) Å with a reduction of –3.37 % in comparison with the sum of the atomic radii of 3.134 Å [16]). Stacking of the cages results in the formation of tunnels along the [010] direction (Fig. 1). The gadolinium atoms are well separated from each other. Nevertheless, the shortest Gd–Gd distance of 3.838(3) Å is only slightly larger than the sum of the atomic radii ($\Delta = 6.4\,\%$) and thus two additional Gd atoms are included in the coordination sphere. Consequently, the gadolinium atoms are surrounded by 17 atoms forming coordination polyhedra (CP) $[GdZn_{15}Gd_2]$ which can be described as a pentagonal prism with seven additional atoms in the equatorial plane (Fig. 2). This polyhedron has no analogs within Gd_xZn_y structures, though the coordination number is between minimal 14 in the Gd-rich phase GdZn [3] and maximal 20 in the Zn-richer phases Gd_3Zn_{11} [1, 2], Gd_3Zn_{22} [1, 2] and $GdZn_{12}$ [1, 2, 10]. Two types of polyhedra are observed for the Zn atoms. Both Zn1 and Zn2 have coordination number (CN) 10 in geometrically similar $[Zn1Zn_6Gd_4]$ and $[Zn2Zn_5Gd_5]$ polyhedra. They can be described as distorted trigonal prisms with three additional atoms on lateral faces and one atom on an edge. Similar coordination polyhedra of Zn atoms are found in the neighboring $GdZn_2$ [4] and Gd_3Zn_{11} [1, 2] phases. Strongly distorted $[Zn3Zn_7Gd_5]$ cuboctahedra are centered by Zn3. It should, however, be noticed that there are two additional atoms at somewhat longer distances of 3.184(4) Å which can be assigned to the second coordination sphere. Such CP exists also in Gd_3Zn_{11}. Twelve is the most common Zn coordination number in the Gd_xZn_y structures, especially in the Zn-rich part, however, with icosahedral motifs. A general tendency to decrease the coordination number of gadolinium and zinc upon an increase of the gadolinium content is observed in the structures of the Gd-Zn binary system.

Though, so far, the YZn_3 type has only five RZn_3 representatives [1], its ternary ordering variants have been found in the systems of rare-earth-transition

metal-*p*-element combinations. The structural relation between $ScRhSi_2$ [17], β-$YbAgGa_2$ [18] and $GdZn_3$ has been described in recent publications. It has been pointed out, that the YZn_3 structure can be obtained from the higher symmetrical Re_3B (or its ordered variant $MgCuAl_2$) where the space group *Cmcm* is lowered to *Pnma* by a *klassengleiche* symmetry reduction of index 2 [18, 19].

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