Monatshefte für Chemie 135, 1327–1334 (2004)
DOI 10.1007/s00706-004-0210-x

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

Ternary Germanides RE_2Ge_2Mg (RE = Y, La–Nd, Sm, Gd, Tb)

Rainer Kraft and **Rainer Pöttgen**[*]

Institut für Anorganische und Analytische Chemie,
Westfälische Wilhelms-Universität Münster, 48149 Münster (Germany)

Received March 11, 2004; accepted (revised) April 7, 2004

Summary. The ternary rare earth metal–magnesium–germanides RE_2Ge_2Mg (RE = Y, La–Nd, Sm, Gd, Tb) were synthesized by reaction of the elements in sealed tantalum tubes in a water-cooled sample chamber of an induction furnace. The germanides were characterized through their X-ray powder patterns. The structures of Ce_2Ge_2Mg and Pr_2Ge_2Mg were refined from X-ray single crystal diffractometer data: Mo_2FeB_2 type, $P4/mbm$, $a = 750.6(1)$, $c = 442.4(1)$ pm, $wR2 = 0.0378$, 386 F^2 values, 12 variable parameters for Ce_2Ge_2Mg, and $a = 745.7(1)$, $c = 439.2(1)$ pm, $wR2 = 0.0462$, 448 F^2 values, 12 variable parameters for Pr_2Ge_2Mg. The lanthanum compound shows a homogeneity range $La_{2+x}Ge_2Mg_{1-x}$. The structure of a single crystal with $x = 0.249(5)$ was refined from X-ray data: $a = 770.52(7)$, $c = 447.4(1)$ pm, $wR2 = 0.0481$, 322 F^2 values, 13 variable parameters. The RE_2Ge_2Mg structures can be considered as a 1:1 intergrowth of CsCl and AlB_2 related slabs of compositions REMg and REGe$_2$.

Keywords. Rare earth compounds; Germanides; Crystal chemistry.

Introduction

More than 200 R_2T_2X compounds (R = rare earth or actinoid metal; T = late transition metal; X = element of the p block) have been synthesized and characterized in the last ten years. These intermetallics crystallize with the tetragonal Mo_2FeB_2 (space group $P4/mbm$) [1] or Er_2Au_2Sn (space group $P4_2/mnm$) [2] type structure. The crystal chemistry and the largely varying physical properties of this peculiar family of compounds have recently been reviewed [3]. The structures can be considered as an intergrowth of slightly distorted AlB_2 and CsCl related slabs. To give an example, the Er_2Au_2Sn structure is composed of $ErAu_2$ and ErSn slabs with Au_2 pairs at a Au–Au distance of 281 pm in the AlB_2 slab.

These intermetallics show manifold magnetic properties like antiferro- or ferromagnetism, *Kondo* and non-*Fermi*-liquid systems and also non-magnetic ground

---

[*] Corresponding author. E-mail: pottgen@uni-muenster.de

states. Remarkable is the intermediate valence in $Ce_2Ni_{1.88}Cd$ [4] and Yb_2Pd_2In [5] and the high electronic specific heat coefficients of $\gamma = 500\,mJ/mol\,K^2$ in Ce_2Pt_2In [6] and of $\gamma = 850\,mJ/mol\,K^2$ in the heavy fermion compound U_2Pt_2In [7].

An important parameter for the type of magnetic ordering and the value of the ordering temperature is the strength of the 4*f* (*RE*)–*d*(*T*) and 5*f* (U)–*d*(*T*) hybridization (*RE* = rare earth element). In this context it is interesting to investigate isotypic compounds, where the transition metal is fully substituted by a main group element. However, only a small number of such intermetallics have been reported, that are RE_2Ge_2In [8], Gd_2Ge_2Mg [9], Ce_2Si_2Mg [10], RE_2Si_2Li (*RE* = Y, Nd) [11], Sc_2Si_2Al [12], and Yb_2Si_2Al [13]. In these silicides and germanides, the silicon and germanium atoms form Si_2 or Ge_2 pairs in the distorted AlB_2 slabs with Si–Si and Ge–Ge distances that resemble those in the elemental structures. So far, we can give only one example for the large influence of the *T*–*p* element substitution, *i.e.* the largely varying magnetic ordering temperatures of 49 K in Gd_2Ni_2Mg [14] and 150 K in Gd_2Ge_2Mg [9].

We have now started a more systematic investigation of such RE_2X_2X' compounds. Herein we report on the synthesis and structural characterization of the ternary germanides RE_2Ge_2Mg with *RE* = Y, La–Nd, Sm, Gd, and Tb.

Results and Discussion

A series of new RE_2Ge_2Mg intermetallics has been synthesized and structurally characterized. The compounds with Y, La, Ce, Pr, Nd, Sm, and Tb are reported here for the first time, while Gd_2Ge_2Mg [9] is already known. Since the crystal chemistry of the large family of U_3Si_2/Mo_2FeB_2 related intermetallics has recently been reviewed in detail [3], we give only a brief account here and focus on chemical bonding and on the homogeneity range of the lanthanum compound. The lattice parameters of the RE_2Ge_2Mg germanides decrease from the lanthanum to the terbium compound as expected from the lanthanoid contraction. The cell volume of Y_2Ge_2Mg is slightly smaller than the volume of the terbium germanide (Fig. 1). The germanides RE_2Ge_2In [8] are isotypic with the RE_2Ge_2Mg series presented here. The cell volumes of the indium compounds are *ca.* 1% larger than those of the magnesium compounds, as expected from the larger metallic radius of indium (166 pm) as compared to magnesium (160 pm) [21].

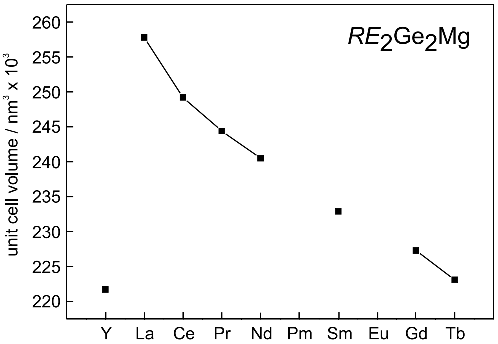

Fig. 1. Plot of the cell volumes of the RE_2Ge_2Mg germanides

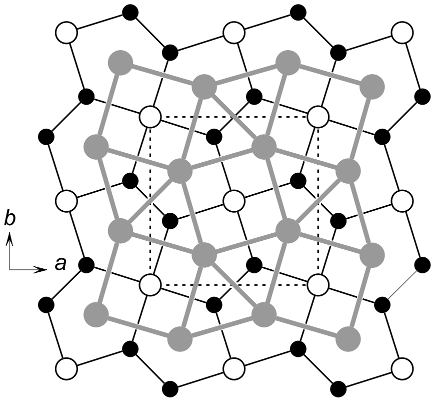

Fig. 2. Projection of the Ce_2Ge_2Mg structure onto the xy plane; all atoms lie on mirror planes at $z = 0$ (Ge, Mg) and $z = 1/2$ (Ce); cerium, germanium, and magnesium atoms are drawn as grey, filled, and open circles, respectively; the CsCl and AlB_2 related slabs and the $[Ge_2Mg]$ network are emphasized

As an example we present the Ce_2Ge_2Mg structure in Fig. 2. The structure can be described as a 1:1 intergrowth of CsCl and AlB_2 related slabs of compositions CeMg and $CeGe_2$. Whereas binary CeMg with CsCl structure is known [22], $CeGe_2$ crystallizes with the well-known α-$ThSi_2$ type [23]. The magnesium and germanium atoms on the mirror plane at $z = 0$ build a two-dimensional $[Ge_2Mg]$ network with Ge–Ge and Ge–Mg distances of 254 and 299 pm, respectively.

The Ge–Ge distance within the Ge_2 dumbbell is similar to isotypic La_2Ge_2In [8] (254 pm) and the *Zintl* phase Eu_5Ge_3 [24] (256 pm). In compounds with germanium chains the Ge–Ge distances are slightly longer, *e.g.* 257 pm in $EuIrGe_2$ [24] or 262 pm in the low-temperature modification of LaGe [25]. At this point it is interesting to compare the $[Ge_2Mg]$ substructure of Ce_2Ge_2Mg with that of the *Zintl* phase Mg_2Ge [26], where each magnesium atom has a tetrahedral germanium coordinations at Mg–Ge distances of 276 pm. The distinct difference between the structures of Ce_2Ge_2Mg and Mg_2Ge is that the magnesium atoms in Ce_2Ge_2Mg have a square-planar germanium coordination.

Chemical bonding in the RE_2Ge_2Mg germanides was investigated recently for Gd_2Ge_2Mg by *Choe et al.* [9]. Assuming that the Ge_2 dimers are isoelectronic with bromine, one can formulate $(2Gd^{3+})Mg^{2+}(Ge_2{}^{6-})(2e^-)$ leaving two surplus electrons. This formulation can only be considered as a first approximation, since the electronic structure calculation revealed also significant Gd–Ge and Mg–Ge interactions. For more details we refer to Ref. [9].

The lanthanum compound is an exception in the series of RE_2Ge_2Mg germanides. The cell volume determined from the *Guinier* powder pattern of the bulk sample fits well into the plot of the cell volumes (Fig. 1). Our single crystal X-ray data, however, gave a hint for a pronounced homogeneity range $La_{2+x}Ge_2Mg_{1-x}$. The a lattice parameter of the single crystals were significantly larger than those of the bulk sample, while the c parameters where more or less similar (Table 1). As discussed earlier [3], the c parameters of the R_2T_2X compounds mainly depend on the size of the R atoms, while the a parameters vary with the size of the T and X atoms forming the two-dimensional $[T_2X]$ networks. Thus, partial substitution of

Table 1. Lattice parameters of the tetragonal germanides RE_2Ge_2Mg (space group $P4/mbm$, Mo_2FeB_2 type)

Compound	a/pm	c/pm	V/nm^3
Y_2Ge_2Mg	723.8(1)	423.2(1)	0.2217
$La_{2.249(5)}Ge_2Mg_{0.751(5)}$[a]	770.52(7)	447.4(1)	0.2656
$La_{2.234(6)}Ge_2Mg_{0.766(6)}$[a]	769.23(7)	447.4(1)	0.2647
La_2Ge_2Mg	757.93(8)	448.82(6)	0.2578
Ce_2Ge_2Mg	750.6(1)	442.4(1)	0.2492
Pr_2Ge_2Mg	745.7(1)	439.2(1)	0.2442
Nd_2Ge_2Mg	742.2(7)	436.4(5)	0.2404
Sm_2Ge_2Mg	734.5(2)	431.8(1)	0.2330
Gd_2Ge_2Mg	728.5(1)	428.2(1)	0.2273
Tb_2Ge_2Mg	725.0(1)	424.6(1)	0.2232

[a] Single crystal diffractometer data

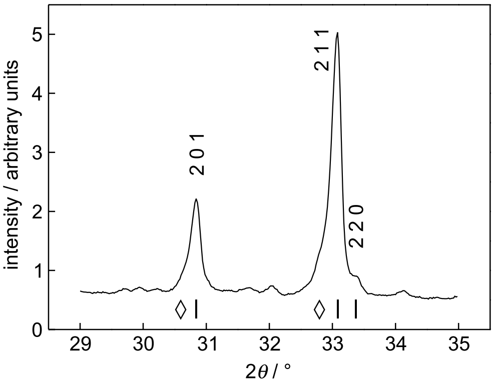

Fig. 3. X-ray powder data (Cu Kα_1 radiation) of the La_2Ge_2Mg sample in the 2θ range from 29 to 35°; the relevant *hkl* indices are given; small vertical lines indicate the positions of the *Bragg* reflections for stoichiometric La_2Ge_2Mg; the rhombs indicate calculated positions of the *Bragg* reflections for the $La_{2.249}Ge_2Mg_{0.751}$ crystal; for details see text

magnesium by lanthanum strongly increases the a parameters. As is evident from Table 1, the crystal with the slightly larger La/Mg mixing shows also a slightly larger a parameter.

Since the two crystals with the higher lanthanum content have been selected from the sample with the starting composition 2La:2Ge:1Mg, we analyzed the X-ray powder pattern in more detail. In Fig. 3 we present a cutout of the powder diagram from $2\theta = 29$–35°. Both the 201 and 211 reflections show clear shoulders at the left-hand side. This is a clear evidence for the homogeneity range. In Fig. 3 we have marked the calculated positions for the 201 and 211 reflections for the $La_{2.249(5)}Ge_2Mg_{0.751(5)}$ crystal. These scale approximately with the maximum of the shoulders. Thus, our sample contained La_2Ge_2Mg as the main phase and additionally some $La_{2+x}Ge_2Mg_{1-x}$. Similar behavior has recently also been observed for the $YbNi_{1-x}Sb$ antimonides [27]. Metallographic analyses of samples of the solid solution $La_{2+x}Ge_2Mg_{1-x}$ with larger x gave even evidence for binary

La_3Ge_2, although this binary germanide has not yet been synthesized in pure form. Further investigations are in progress. Finally it is worthwhile to note that based on the X-ray powder and EDX data, a homogeneity range is only observed for the lanthanum compound.

Experimental

Synthesis

Starting materials for the preparation of the RE_2Ge_2Mg germanides were ingots of the rare earth metals (Johnson Matthey, Chempur or Kelpin, $> 99.9\%$), germanium lumps (Wacker, $> 99.9\%$), and a magnesium rod (Johnson Matthey, Ø 16 mm, $> 99.5\%$). The rare earth metal pieces were first melted under 600 mbar argon to small buttons in an arc-melting furnace [15]. The argon was purified over titanium sponge (900 K), silica gel, and molecular sieves. Pieces of the magnesium rod (the surface of the rod was first cut on a turning lathe in order to remove surface impurities), the arc-melted rare earth metal buttons and powder of the germanium lumps were then weighed in the ideal 2*RE*:2Ge:1Mg atomic ratios and sealed in tantalum ampoules (*ca.* 1 cm^3 tube volume) under an argon pressure of about 800 mbar.

The tantalum tubes were placed in a water-cooled sample chamber [16] of an induction furnace (Hüttinger Elektronik, Freiburg, Typ TIG 1.5/300), first heated for 15 minutes at about 1500 K and subsequently annealed for another 4 hours at *ca.* 1070 K. Finally the tube was quenched to room temperature by switching off the power of the generator. The brittle products could readily be separated from the tubes. No reaction with the tantalum container could be observed. Small single crystals were available directly from these annealing procedures. In some cases, especially for the lanthanum compound, small amounts of volatile magnesium had distilled at the upper, colder part of the tantalum tubes. This leads to lower magnesium content in the sample. For details see the discussion section.

Compact pieces and powders of the germanides are stable in air over months. Powders are dark grey and single crystals exhibit metallic lustre.

Scanning Electron Microscopy

The La_2Ge_2Mg and 2.5La:2Ge:0.5Mg bulk samples and the two $La_{2+x}Ge_2Mg_{1-x}$ single crystals investigated on the diffractometer have been analyzed by EDX measurements using a LEICA 420 I scanning electron microscope with LaB_6, germanium, and MgO as standards. The bulk samples were previously embedded in a metacrylate matrix and the surface was polished with a diamond paste. The surface remained unetched for the EDX measurements. No impurity elements were detected. Various point analyses of the bulk sample mainly revealed the ideal La_2Ge_2Mg composition, however, some parts of the sample showed a higher lanthanum content, *i.e.* 49 ± 2 at.-% La: 39 ± 2 at.-% Ge: 12 ± 2 at.-% Mg. Similar results were obtained for the two single crystals. Since the crystals on the glass fibres were irregularly shaped, the various point analyses revealed different results, but in all cases, the lanthanum content was higher than 40 at.-% and the magnesium content always smaller than 20 at.-%, in agreement with the refined compositions (see below). Analysis of the 2.5La:2Ge:0.5Mg sample also revealed some areas which contained no magnesium. The compositions were 60 ± 2 at.-% La: 40 ± 2 at.-% Ge.

X-Ray Film Data and Structure Refinements

The samples were characterized through their *Guinier* powder patterns using Cu $K\alpha_1$ radiation and α-quartz ($a = 491.30$, $c = 540.46$ pm) as an internal standard. The *Guinier* camera was equipped with an imaging plate system (Fujifilm BAS–1800). The tetragonal lattice parameters (Table 1) were obtained from least-squares fits of the *Guinier* data. To ensure correct indexing, the observed patterns were compared to calculated ones [17] using the atomic positions obtained from the structure refinements. Except the lanthanum compounds (see below), the lattice parameters derived for the powders and the single crystals agreed well. For Gd_2Ge_2Mg our lattice parameters show good agreement with the data from *Choe et al.* [9] of $a = 729.1(1)$ and $c = 428.26(8)$ pm.

The *Guinier* powder data and the occupancy parameters derived from the single crystal study (see below) revealed a homogeneity range for the lanthanum compound. Subsequently, the La_2Ge_2Mg sample has also been studied on a Stoe Stadi P powder diffractometer with Ge monochromated Cu $K\alpha_1$ radiation. The measurement was performed in transmission geometry (sample mounted on a mylar foil with greese) within the 2θ range 29–35° in steps of 0.02° (2θ) with a total counting time of 15 h.

Irregularly shaped single crystals of $La_{2+x}Ge_2Mg_{1-x}$, Ce_2Ge_2Mg, and Pr_2Ge_2Mg were isolated from the annealed samples by mechanical fragmentation and subsequently examined by *Laue* photographs on a *Buerger* precession camera (equipped with an imaging plate system Fujifilm BAS–1800) in order to establish suitability for intensity data collection. Intensity data of $La_{2.249(5)}Ge_2Mg_{0.751(5)}$, $La_{2.234(6)}Ge_2Mg_{0.766(6)}$, Ce_2Ge_2Mg, and Pr_2Ge_2Mg were recorded at room temperature by use of a four-circle diffractometer (CAD4) with graphite monochromatized Mo $K\alpha$ radiation ($\lambda = 71.073$ pm) and a scintillation counter with pulse-height discrimination. The scans were taken in the $\omega/2\theta$ mode and empirical absorption corrections were applied on the basis of psi-scan data. All relevant crystallographic data for the data collections and evaluations are listed in Table 2. Since the results for the two lanthanum containing crystals were identical within two combined standard deviations, only the data of $La_{2.249(5)}Ge_2Mg_{0.751(5)}$ are reported here.

The isotypy of RE_2Ge_2Mg germanides with the RE_2T_2Mg intermetallics [18, 19] was already evident from the X-ray powder data. The atomic positions of La_2Cu_2Mg [18] were taken as starting

Table 2. Crystal data and structure refinement for $La_{2.249(5)}Ge_2Mg_{0.751(5)}$, Ce_2Ge_2Mg, and Pr_2Ge_2Mg (space group $P4/mbm$; Z = 2)

Empirical formula	$La_{2.249(5)}Ge_2Mg_{0.751(5)}$	Ce_2Ge_2Mg	Pr_2Ge_2Mg
Molar mass/g mol^{-1}	447.31	449.73	451.31
Unit cell dimensions	$a = 770.52(7)$ pm	$a = 750.6(1)$ pm	$a = 745.7(1)$ pm
	$c = 447.4(1)$ pm	$c = 442.4(1)$ pm	$c = 439.2(1)$ pm
Calculated density	5.59 g/cm^3	5.99 g/cm^3	6.14 g/cm^3
Crystal size/μm^3	10 × 40 × 40	25 × 35 × 40	10 × 30 × 60
Transm. ratio (max/min)	1.78	2.13	1.86
Absorption coefficient/mm^{-1}	26.9	29.8	31.7
$F(000)$	380	384	388
θ range/°	3 to 35	3 to 40	3 to 40
Range in *hkl*	±12, ±12, +5	±12, ±12, ±7	±13, ±13, +7
Total no. reflections	2134	4429	3131
Independent reflections	322 ($R_{int} = 0.0945$)	386 ($R_{int} = 0.0903$)	448 ($R_{int} = 0.0889$)
Reflections with $I > 2\sigma(I)$	250 ($R_{sigma} = 0.0474$)	325 ($R_{sigma} = 0.0340$)	390 ($R_{sigma} = 0.0358$)
Data/parameters	322/13	386/12	448/12
Goodness-of-fit on F^2	1.042	1.151	1.063
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0266$	$R1 = 0.0215$	$R1 = 0.0219$
	$wR2 = 0.0434$	$wR2 = 0.0354$	$wR2 = 0.0445$
R indices (all data)	$R1 = 0.0492$	$R1 = 0.0341$	$R1 = 0.0303$
	$wR2 = 0.0481$	$wR2 = 0.0378$	$wR2 = 0.0462$
Extinction coefficient	0.012(1)	0.0041(5)	0.0053(6)
Largest diff. peak and hole/eÅ^{-3}	1.66 and −1.54	1.63 and −1.64	2.77 and −1.61

values and the structures were successfully refined using SHELXL-97 (full-matrix least-squares on F_o^2) [20] with anisotropic atomic displacement parameters for all sites.

The displacement parameter of the magnesium positions of the lanthanum containing compounds were much too small, indicating a larger scattering power for these positions. Both lanthanum and germanium have a larger scattering power, and consequently Mg/La or Mg/Ge mixing is possible. The *a* lattice parameters of the single crystals are significantly larger than those for the bulk sample as determined from X-ray powder diffraction (Table 1). In view of the metallic radii of La (187 pm), Mg (160 pm), and Ge (137 pm) [21], only Mg/La mixing is reasonable for the 2*a* site. This is also consistent with our phase analytical investigations. In the final cycles, the mixed Mg/La occupancy for the 2*a* site was refined as a least-squares variable. For Ce_2Ge_2Mg and Pr_2Ge_2Mg all sites are fully occupied within two standard deviations. In the last cycles, the ideal occupancies were assumed again. Final difference *Fourier* synthesis revealed no significant residual peaks (see Table 2). The positional parameters and interatomic distances are listed in Tables 3 and 4. Listings of the observed and calculated structure factors are available at Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry No's. CSD–413848 ($La_{2.249}Ge_2Mg_{0.751}$), CSD–413849 (Ce_2Ge_2Mg), and CSD–413850 (Pr_2Ge_2Mg).

Table 3. Atomic coordinates and isotropic displacement parameters (pm^2) for $La_{2.249(5)}Ge_2Mg_{0.751(5)}$, Ce_2Ge_2Mg, and Pr_2Ge_2Mg (space group *P*4/*mbm*); U_{eq} is defined as a third of the trace of the orthogonalized U_{ij} tensor

Atom	*Wyckoff* site	*x*	*y*	*z*	U_{eq}
$La_{2.249(5)}Ge_2Mg_{0.751(5)}$					
La	4*h*	0.17852(5)	1/2 + *x*	1/2	93(2)
Ge	4*g*	0.38244(9)	1/2 + *x*	0	96(2)
Mg/La[a]	2*a*	0	0	0	177(8)
Ce_2Ge_2Mg					
Ce	4*h*	0.17852(3)	1/2 + *x*	1/2	58(1)
Ge	4*g*	0.38016(7)	1/2 + *x*	0	65(1)
Mg	2*a*	0	0	0	98(6)
Pr_2Ge_2Mg					
Pr	4*h*	0.17829(3)	1/2 + *x*	1/2	51(1)
Ge	4*g*	0.37965(6)	1/2 + *x*	0	55(1)
Mg	2*a*	0	0	0	93(6)

[a] This site shows mixed occupancy: 75.1(5)% Mg and 24.9(5)% La

Table 4. Interatomic distances (pm) in the structure of Ce_2Ge_2Mg, calculated with the lattice parameters taken from X-ray powder data; standard deviations are given in parenthesis

Ce: 2	Ge	307.80(7)	Ge: 1	Ge	254.4(1)
4	Ge	317.84(5)	2	Mg	299.19(5)
4	Mg	353.71(4)	2	Ce	307.80(7)
1	Ce	379.00(8)	4	Ce	317.84(5)
4	Ce	390.34(5)	Mg: 4	Ge	299.19(5)
2	Ce	442.4(1)	8	Ce	353.71(4)

Acknowledgements

We thank *B. Heying* and Dipl.-Ing. *U. Ch. Rodewald* for the intensity data collections and *H.-J. Göcke* for the work at the scanning electron microscope. This work was financially supported by the Deutsche Forschungsgemeinschaft.

References

[1] Rieger W, Nowotny H, Benesovsky F (1964) Monatsh Chem **95**: 1502
[2] Pöttgen R (1994) Z Naturforsch **49b**: 1309
[3] Lukachuk M, Pöttgen R (2003) Z Kristallogr **218**: 767
[4] Niepmann D, Pöttgen R, Künnen B, Kotzyba G (2000) J Solid State Chem **150**: 134
[5] Giovannini M, Bauer E, Michor H, Hilscher G, Galatanu A, Saccone A, Rogl P (2001) Intermetallics **9**: 481
[6] Hauser R, Michor H, Bauer E, Hilscher G, Kaczorowski D (1997) Physica B **230–232**: 211
[7] Havela L, Sechovský V, Svoboda P, Nakotte H, Prokeš K, deBoer FR, Seret A, Winand JM, Rebizant J, Spirlet JC, Purwanto A, Robinson RA (1995) J Magn Magn Mater **140–144**: 1367
[8] Zaremba VI, Stepien'-Damm A, Nichiporuk GP, Tyvanchuk YuB, Kalychak YaM (1998) Crystallogr Rep **43**: 8
[9] Choe W, Miller GJ, Levin EM (2001) J Alloys Compd **329**: 121
[10] Dhar SK, Manfrinetti P, Palenzona A (1997) J Alloys Compd **252**: 24
[11] Steinberg G, Schuster H-U (1979) Z Naturforsch **34b**: 1237
[12] Tyvanchuk AT, Yanson TI, Kotur BYA, Zarechnyuk O (1988) Izv Akad Nauk SSSR Metally **4**: 187
[13] Krahnenberg C, Mewis A (2000) Z Anorg Allg Chem **626**: 1448
[14] Łątka K, Kmieć R, Pacyna AW, Mishra R, Pöttgen R (2001) Solid State Sci **3**: 545
[15] Pöttgen R, Gulden Th, Simon A (1999) GIT Labor Fachzeitschrift **43**: 133
[16] Kußmann D, Hoffmann R-D, Pöttgen R (1998) Z Anorg Allg Chem **624**: 1727
[17] Yvon K, Jeitschko W, Parthé E (1977) J Appl Crystallogr **10**: 73
[18] Mishra R, Hoffmann R-D, Pöttgen R (2001) Z Naturforsch **56b**: 239
[19] Kraft R, Fickenscher Th, Kotzyba G, Hoffmann R-D, Pöttgen R (2003) Intermetallics **11**: 111
[20] Sheldrick GM (1997) SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen
[21] Emsley J (1999) The Elements. Oxford University Press, Oxford
[22] Nowotny H (1942) Z Metallkd **34**: 247
[23] Gladyshevskii EI (1964) J Struct Chem **5**: 523
[24] Pöttgen R, Simon A (1996) Z Anorg Allg Chem **622**: 779
[25] Mattausch HJ, Simon A (2004) Z Naturforsch **59b**: 559
[26] Glazov VM, Glagoleva NN (1965) Inorg Mater **1**: 989
[27] Mishra R, Pöttgen R, Hoffmann R-D, Fickenscher Th, Eschen M, Trill H, Mosel BD (2002) Z Naturforsch **57b**: 1215