Ternary Rare Earth Transition Metal Zinc Compounds $Ln_2T_3Zn_{14}$ (T = Fe, Co, Rh, Ni, Pd, Pt) with Ordered Th_2Zn_{17}-Type Structure and Structure Refinement of the Corresponding Binary Compound La_2Zn_{17}

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Fifty new ternary compounds $Ln_2T_3Zn_{14}$ were isolated from alloys with a high zinc content by dissolving the zinc-rich matrix in hydrochloric acid. They crystallize with an ordered version of a binary structure type first reported for Th_2Zn_{17}. The structure of the ternaries was determined from four-circle X-ray diffractometer data of the four compounds $Gd_2Co_3Zn_{14}$, $Ce_2Rh_3Zn_{14}$, $Pr_2Ni_3Zn_{14}$, and $Sm_2Pd_3Zn_{14}$. It is rhombohedral, space group $R\bar{3}m$, with $Z = 3$ formula units in the corresponding hexagonal cell and the lattice constants $a = 887.2(2)$ pm and $c = 1300.2(3)$ pm for $Gd_2Co_3Zn_{14}$. The transition metal atoms T are located essentially at one atomic site corresponding to the ideal occupancy in the compounds $Gd_2Co_3Zn_{14}$ and $Pr_2Ni_3Zn_{14}$. For the other two compounds significant deviations from the ideal composition could be observed for three of the four zinc sites of Th_2Zn_{17}, with mixed T/Zn occupancy, resulting in the compositions $Ce_2Rh_{1.90(2)}Zn_{15.10(2)}$ and $Sm_2Pd_{1.92(1)}Zn_{15.08(1)}$. The structure may be viewed as consisting of layers extending perpendicular to the hexagonal axis. One layer contains all of the rare earth atoms, the other all of the transition metal atoms, and both with additional zinc atoms, with unit mesh contents of Ln_2Zn_6 and T_3Zn_8. These layers alternate, corresponding to the formula $Ln_2Zn_6 \cdot T_3Zn_8 = Ln_2T_3Zn_{14}$. The structure contains two kinds of voids. One of these is filled by carbon and nitrogen atoms in ternary magnetic materials $Ln_2Fe_{17}C_{3-x}$ and $Ln_2Fe_{17}N_{3-x}$. The structure refinements show that both of these voids are unoccupied in the ternary zinc compounds $Ln_2T_3Zn_{14}$. Similarly, a structure refinement of the known binary compound La_2Zn_{17} did not reveal any significant amounts of impurity atoms (e.g., oxygen) at these voids. The refinement of the occupancy parameters for this compound resulted in the composition $La_2Zn_{16.06(6)}$.

Introduction

We have recently characterized a large number of ternary compounds with a high content of zinc. Some fifty rare earth transition metal zinc compounds LnT_2Zn_{20} with T = Fe, Ru, Co, Rh, and Ni were found to crystallize with $CeCr_2Al_{20}$-type structure.[1] This structure was also found for several compounds of the composition TT'_2Zn_{20} with T = Zr, Hf, and Nb and T' = Mn, Fe, Ru, Co, Rh, and Ni.[2] Such compounds may occur in zinc alloys as undesired impurities. However, they could also improve the mechanical properties of such materials as has been reported for corresponding aluminum alloys.[3,4] Another materials science aspect of the present work is the fact that ternary interstitial carbides $Ln_2Fe_{17}C_{3-x}$ and nitrides $Ln_2Fe_{17}N_{3-x}$ with the binary Th_2Zn_{17} type as host structure have become valuable as magnetic materials.[5,6]

Experimental Section

Sample Preparation. Starting materials for the preparation of the compounds $Ln_2T_{3-x}Zn_{14+x}$ were the elemental metals, all with nominal purities >99.9%. The transition metals were mostly bought as powders with the exception of zinc, which was in the form of cut ingots. The light lanthanoid metals were purchased as ingots under dry (sodium) paraffin oil, which was washed away by dry *n*-hexane prior to the reactions. The other lanthanoids were used in the form of turnings.

The compounds were prepared by reaction of the elements usually in the atomic ratio Ln:T:Zn = 2:3:20. The lanthanoid metals were cold-pressed to pellets together with the transition metals (without zinc). These pellets were reacted in an arc-melting furnace. The resulting binary compounds were ground to powders and mixed with zinc. This mixture was cold-pressed to pellets, sealed into evacuated silica tubes, and annealed for 120 h at 850 °C. The ampules were then slowly cooled (5 °C/h) to 500 °C and annealed further for 240 h at that temperature, followed by quenching in ice water.

The binary compound La_2Zn_{17} was prepared from lanthanum pieces and zinc powder. These components were pressed to pellets and melted in evacuated sealed silica tubes. The

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Table 1. Lattice Constants of Ternary Compounds with the Hexagonal Ordered Th_2Zn_{17}-Type Structure[a]

compound	a (pm)	c (pm)	c/a	V (nm³)	compound	a (pm)	c (pm)	c/a	V (nm³)
$La_2Fe_3Zn_{14}$	912.7(3)	1334.1(4)	1.4617	0.9624	$Nd_2Rh_{3-x}Zn_{14+x}$	902.3(2)	1319.3(3)	1.4622	0.9302
$Ce_2Fe_3Zn_{14}$	908.4(2)	1327.9(3)	1.4618	0.9490	$Sm_2Rh_{3-x}Zn_{14+x}$	900.8(2)	1316.7(3)	1.4617	0.9253
$Pr_2Fe_3Zn_{14}$	905.8(2)	1326.0(3)	1.4639	0.9422	$La_2Ni_3Zn_{14}$	899.8(1)	1320.3(2)	1.4673	0.9256
$Nd_2Fe_3Zn_{14}$	904.5(2)	1323.3(3)	1.4630	0.9375	$Ce_2Ni_3Zn_{14}$	896.4(2)	1316.5(3)	1.4687	0.9161
$Sm_2Fe_3Zn_{14}$	899.5(2)	1320.2(1)	1.4677	0.9251	$Pr_2Ni_3Zn_{14}$	895.9(2)	1316.5(3)	1.4695	0.9152
$Gd_2Fe_3Zn_{14}$	896.5(2)	1315.0(3)	1.4668	0.9154	$Nd_2Ni_3Zn_{14}$	895.2(1)	1310.6(2)	1.4640	0.9096
$Tb_2Fe_3Zn_{14}$	895.0(2)	1313.9(3)	1.4680	0.9115	$Sm_2Ni_3Zn_{14}$	891.6(2)	1305.7(3)	1.4644	0.8989
$Dy_2Fe_3Zn_{14}$	892.5(3)	1312.5(4)	1.4706	0.9055	$Gd_2Ni_3Zn_{14}$	887.2(3)	1303.7(4)	1.4695	0.8886
$Ho_2Fe_3Zn_{14}$	892.5(2)	1310.2(2)	1.4680	0.9039	$Tb_2Ni_3Zn_{14}$	886.0(2)	1302.2(2)	1.4698	0.8852
$Er_2Fe_3Zn_{14}$	891.4(2)	1310.0(2)	1.4696	0.9015	$Dy_2Ni_3Zn_{14}$	884.9(3)	1301.1(5)	1.4703	0.8823
$Tm_2Fe_3Zn_{14}$	890.6(1)	1308.5(2)	1.4693	0.8989	$Ho_2Ni_3Zn_{14}$	883.3(2)	1299.5(2)	1.4712	0.8782
$La_2Co_3Zn_{14}$	902.1(2)	1328.6(2)	1.4728	0.9363	$Er_2Ni_3Zn_{14}$	883.2(2)	1297.8(3)	1.4694	0.8766
$Ce_2Co_3Zn_{14}$	899.5(1)	1327.8(2)	1.4762	0.9304	$Tm_2Ni_3Zn_{14}$	880.7(2)	1293.3(3)	1.4685	0.8688
$Pr_2Co_3Zn_{14}$	898.5(1)	1324.8(1)	1.4745	0.9261	$La_2Pd_{3-x}Zn_{14+x}$	912.4(2)	1336.6(2)	1.4649	0.9635
$Nd_2Co_3Zn_{14}$	897.0(1)	1321.0(2)	1.4727	0.9204	$Ce_2Pd_{3-x}Zn_{14+x}$	908.3(2)	1330.6(3)	1.4649	0.9507
$Sm_2Co_3Zn_{14}$	893.3(2)	1316.5(3)	1.4737	0.9098	$Pr_2Pd_{3-x}Zn_{14+x}$	906.5(3)	1330.4(4)	1.4676	0.9468
$Gd_2Co_3Zn_{14}$	890.7(3)	1309.5(5)	1.4702	0.8997	$Nd_2Pd_{3-x}Zn_{14+x}$	904.8(2)	1328.0(3)	1.4677	0.9416
$Tb_2Co_3Zn_{14}$	889.6(4)	1305.9(5)	1.4680	0.8950	$Sm_2Pd_{3-x}Zn_{14+x}$	902.2(2)	1324.0(3)	1.4675	0.9332
$Dy_2Co_3Zn_{14}$	888.2(4)	1304.8(6)	1.4690	0.8915	$Gd_2Pd_{3-x}Zn_{14+x}$	898.5(3)	1318.7(5)	1.4677	0.9221
$Ho_2Co_3Zn_{14}$	887.1(4)	1302.7(6)	1.4685	0.8879	$Tb_2Pd_{3-x}Zn_{14+x}$	897.3(3)	1318.8(3)	1.4697	0.9195
$Er_2Co_3Zn_{14}$	885.6(3)	1303.0(5)	1.4713	0.8851	$Dy_2Pd_{3-x}Zn_{14+x}$	896.2(1)	1317.9(2)	1.4705	0.9166
$Tm_2Co_3Zn_{14}$	883.9(2)	1299.6(3)	1.4703	0.8794	$Ho_2Pd_{3-x}Zn_{14+x}$	895.0(2)	1316.0(3)	1.4704	0.9129
$La_2Rh_{3-x}Zn_{14+x}$	909.2(2)	1331.6(3)	1.4646	0.9533	$Er_2Pd_{3-x}Zn_{14+x}$	894.8(1)	1315.1(2)	1.4697	0.9119
$Ce_2Rh_{3-x}Zn_{14+x}$	905.9(1)	1327.7(2)	1.4656	0.9437	$Tm_2Pd_{3-x}Zn_{14+x}$	893.5(2)	1314.1(3)	1.4707	0.9086
$Pr_2Rh_{3-x}Zn_{14+x}$	904.5(2)	1324.6(3)	1.4645	0.9386	$Gd_2Pt_{3-x}Zn_{14+x}$	899.6(1)	1317.2(2)	1.4642	0.9232

[a] Standard deviations in the place values of the last listed positions are given in parentheses throughout the paper.

Table 2. Crystal Data for $Gd_2Co_3Zn_{14}$, $Ce_2Rh_{3-x}Zn_{14+x}$, $Pr_2Ni_3Zn_{14}$, and $Sm_2Pd_{3-x}Zn_{14+x}$ with Ordered Th_2Zn_{17}-Type Structure and the Corresponding Binary Compound La_2Zn_{17-x} (Space Group $R\bar{3}m$, No. 166, $Z = 3$)′

compound	$Gd_2Co_3Zn_{14}$	$Ce_2Rh_{1.90(2)}Zn_{15.10(2)}$	$Pr_2Ni_3Zn_{14}$	$Sm_2Pd_{1.92(1)}Zn_{15.08(1)}$	$La_2Zn_{16.06(6)}$
lattice constants					
a (pm)	887.2(1)	905.2(1)	895.4(2)	901.3(5)	912.5(1)
c (pm)	1300.2(2)	1328.8(3)	1315.9(2)	1324.2(8)	1333.0(3)
V (nm³)	0.8863	0.9429	0.9137	0.9316	0.9612
formula mass	1406.6	1463.1	1373.2	1490.9	1327.8
calculated density (g/cm³)	7.91	7.73	7.49	7.97	6.88
crystal size (μm)	20 × 20 × 50	40 × 50 × 75	40 × 50 × 75	40 × 50 × 75	75 × 175 × 75
scans up to 2θ	70°	65°	70°	70°	65°
range in h, k, l	±12, ±12, ±20	±13, ±13, −20 to 8	±14, ±14, −8 to 21	±14, ±14, ±21	±13, ±13, 0 to 20
total number of reflections	5269	5848	3358	5430	3804
highest/lowest transmission	1.64	1.48	1.64	1.83	1.79
unique reflections	505	446	518	529	314
internal residual, R_i (on I)	0.039	0.078	0.083	0.078	0.052
reflections with $I_o > 2\sigma(I_o)$	379	333	436	416	280
number of variables	23	27	23	27	25
conventional residual, $R(F_o > 2\sigma)$	0.018	0.022	0.020	0.017	0.026
weighted residual, R_w (all F^2 values)	0.041	0.041	0.048	0.041	0.069
highest/lowest residual electron density (e/Å³)	2.1/−1.1	2.8/−2.6	2.5/−1.4	1.1/−1.5	1.4/−1.7

ampules were annealed at 1110 °C for 1 h, followed by quenching in water.

A problem with the preparation of intermetallics with a high zinc content in silica tubes is the tendency of unreacted zinc to accumulate at the upper (cooler) ends of the sample tubes. This is ascribed to the relatively high vapor pressure of zinc. The problem can be avoided by shaking the tubes in the furnace 2−3 times/day during the whole annealing time as long as there is liquid metal in the tube. Another way of avoiding this problem is to keep the reaction volume in the silica tubes as small as possible. This can be achieved by inserting a fitting silica cylinder on top of the sample in the silica tube proir to sealing.

After the annealing, the excess zinc could frequently be separated from the samples mechanically. Nevertheless, the crushed ingots were treated in diluted hydrochloric acid to remove any remaining zinc. The ternary samples containing the late transition metals are attacked by hydrochloric acid at a much slower rate.

Compact pieces of the compounds show silvery metallic luster; the powders are gray. They are stable in air for long periods of time. Energy-dispersive X-ray fluorescence analyses in a scanning electron microscope did not reveal any impurity elements heavier than sodium.

Structure Refinements. Guinier powder patterns of all samples were recorded with Cu $K\alpha_1$ radiation using α-quartz ($a = 491.30$ pm, $c = 540.46$ pm) as an internal standard. To facilitate the identification of the diffraction lines, we compared the observed patterns to the ones calculated[7] assuming positional parameters as obtained from the single-crystal structure determinations of isotypic compounds with similar composition. The lattice constants (Tables 1 and 2) were refined by least-squares fits. The cell volumes of these compounds are plotted in Figure 1.

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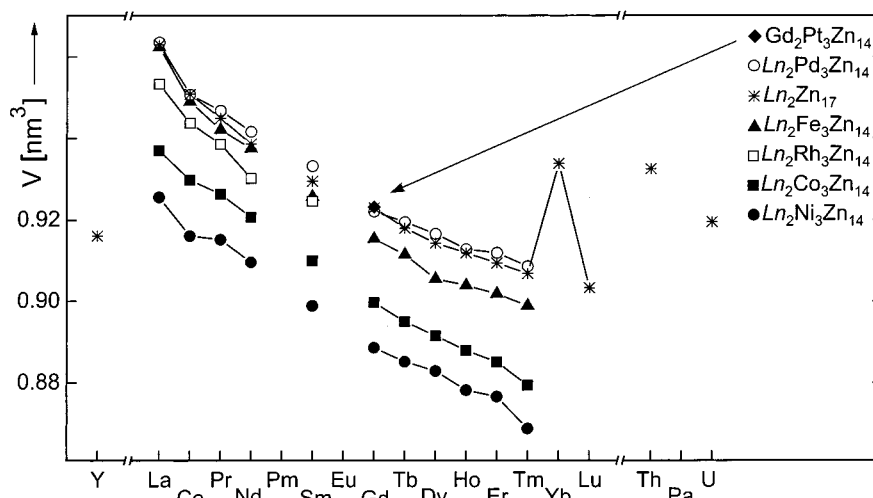
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Figure 1. Cell volumes of binary and ternary compounds with Th_2Zn_{17}-type structure.

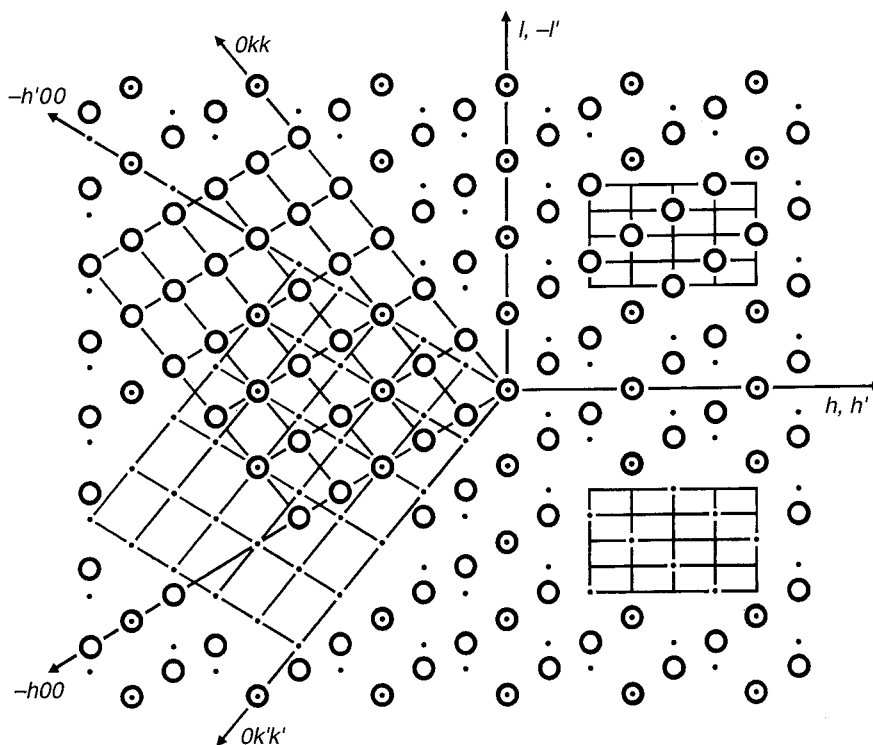**Figure 2.** Reciprocal lattice of a twinned crystal of La_2Zn_{17-x} as observed on a precession diagram. On the left-hand side, the indices hkk and $h'k'k'$ of the rhombohedral cells of the two interpenetrating lattices are shown. On the right-hand side, the reflections are assigned the indices in the hexagonal setting of these lattices. It can be seen that only reflections with $l = 3n$ are common to the lattices of both twin domains.

Single crystals of $Gd_2Co_3Zn_{14}$, $Ce_2Rh_{3-x}Zn_{14+x}$, $Pr_2Ni_3Zn_{14}$, $Sm_2Pd_{3-x}Zn_{14+x}$, and La_2Zn_{17-x} were isolated from the samples and selected for the X-ray data collections on the basis of Laue patterns. The intensity data were recorded on a four-circle diffractometer (Enraf-Nonius, CAD4) with graphite-monochromated Mo $K\alpha$ radiation and a scintillation counter with pulse-height discrimination. The scans were along the Laue streaks ($\theta/2\theta$) with background counts at both ends of each scan. Empirical absorption corrections were made on the basis of ψ-scans. Further details concerning the data collections are listed in Table 2.

The structures were recognized to be isotypic with Th_2Zn_{17}[8] on the basis of their Guinier powder patterns. This was confirmed during the full-matrix least-squares refinements with atomic scattering factors, corrected for anomalous dispersion as provided by the program system.[9] The weighting schemes included a term which accounted for the counting statistics and a parameter correcting for isotropic secondary extinction was optimized as a least-squares variable.

The data set obtained from the specimen of La_2Zn_{17-x} turned out to be collected from a twinned crystal. This was recognized by the observation of systematic non-space-group extinctions of the seemingly primitive hexagonal lattice. On the other hand, the space group of the Th_2Zn_{17}-type structure is rhombohedral. Thus, only reflections with $-h + k + l = 3n$ should be observed. The twinning is illustrated in Figure 2, which shows two interpenetrating reciprocal lattices of a multiple

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Table 3. Atomic Parameters of $Gd_2Co_3Zn_{14}$, $Ce_2Rh_{3-x}Zn_{14+x}$, $Pr_2Ni_3Zn_{14}$, $Sm_2Pd_{3-x}Zn_{14+x}$, and La_2Zn_{17-x}[a]

atom	$R\bar{3}m$	occupancy	x	y	z	B_{eq}
			$Gd_2Co_3Zn_{14}$			
Gd	6c	1	0	0	0.33719(1)	0.667(2)
Co	9d	1.009(2)	$1/2$	0	$1/2$	0.53(1)
Zn1	18h	0.990(3)	0.50065(1)	$-x$	0.15156(2)	0.820(8)
Zn2	18f	0.989(3)	0.29411(2)	0	0	0.874(8)
Zn3	6c	0.986(2)	0	0	0.10453(3)	0.92(1)
			$Ce_2Rh_{1.90(2)}Zn_{15.10(2)}$			
Ce	6c	1	0	0	0.33803(2)	0.679(8)
Rh/Zn	9d	0.525(2)/0.475	$1/2$	0	$1/2$	0.69(1)
Zn1/Rh	18h	0.965(2)/0.035	0.49965(1)	$-x$	0.15214(2)	0.89(1)
Zn2/Rh	18f	0.980(2)/0.020	0.29265(3)	0	0	0.85(1)
Zn3	6c	1.001(1)	0	0	0.10224(3)	0.82(2)
			$Pr_2Ni_3Zn_{14}$			
Pr	6c	1	0	0	0.33815(1)	0.508(4)
Ni	9d	1.005(2)	$1/2$	0	$1/2$	0.59(1)
Zn1	18h	0.998(3)	0.50112(1)	$-x$	0.15209(1)	0.859(8)
Zn2	18f	0.999(3)	0.29236(2)	0	0	0.786(6)
Zn3	6c	0.998(2)	0	0	0.10285(2)	0.90(1)
			$Sm_2Pd_{1.92(1)}Zn_{15.08(1)}$			
Sm	6c	1	0	0	0.33779(1)	0.622(4)
Pd/Zn	9d	0.534(2)/0.466	$1/2$	0	$1/2$	0.697(6)
Zn1/Pd	18h	0.957(1)/0.043	0.49754(1)	$-x$	0.15227(1)	0.856(6)
Zn2/Pd	18f	0.991(1)/0.009	0.29636(2)	0	0	0.824(6)
Zn3	6c	0.999(1)	0	0	0.10144(2)	0.89(1)
			$La_2Zn_{16.06(6)}$			
La	6c	1	0	0	0.33634(3)	0.53(2)
Zn4	9d	0.904(8)	$1/2$	0	$1/2$	0.99(4)
Zn1	18h	0.892(8)	0.49664(7)	$-x$	0.15294(14)	0.85(3)
Zn2	18f	1.002(7)	0.29127(11)	0	0	0.90(2)
Zn3	6c	0.997(9)	0	0	0.09832(9)	0.95(2)

[a] The positional parameters were standardized with the program STRUCTURE TIDY.[12] The third column lists occupancy parameters, which generally were obtained in previous least-squares cycles. In the final cycles the ideal occupancy parameters were used with the exceptions of those for the 9d, 18h, and 18f positions of $Ce_2Rh_{3-x}Zn_{14+x}$ and $Sm_2Pd_{3-x}Zn_{14+x}$, where mixed occupancies were allowed in the final refinement cycles, as is discussed in the text. The results of these cycles are listed here. In the last least-squares cycles for La_2Zn_{17-x} variable occupancies for the Zn1 and Zn4 positions were allowed; the other three positions were refined with ideal occupancies. The last column contains the equivalent isotropic displacement parameters ($\times 10^4$ pm^2) of the corresponding anisotropic parameters.

domain crystal of La_2Zn_{17-x}. It can be seen that only reflections with $l = 3n$ are common to both lattices. These were assigned zero weight in the final least-squares cycles of La_2Zn_{17-x}. Thus, the structure could be refined with one scale factor. Twinning has frequently been observed in Th_2Zn_{17}-type crystals.[10,11] Fortunately, this was not observed during the structure refinements for the ternary compounds $Ln_2T_3Zn_{14}$ investigated by us.

To check for deviations from the ideal compositions, occupancy parameters were refined together with variable anisotropic displacement parameters in separate series of least-squares cycles for all compounds. As can be seen from the results listed in Table 3, no great deviations from the ideal occupancy values were found for the refinements of $Gd_2Co_3Zn_{14}$ and $Pr_2Ni_3Zn_{14}$. In contrast, the occupancies for the 9d, 18h, and 18f positions of $Ce_2Rh_{3-x}Zn_{14+x}$ and $Sm_2Pd_{3-x}Zn_{14+x}$ deviated from the ideal values. Therefore, mixed occupancies were allowed for these positions, while for all other positions the ideal occupancy parameters were assumed during the final least-squares cycles. The final difference Fourier analyses showed no significant electron densities at sites suitable for additional atomic sites. The final residuals, atomic parameters, and the interatomic distances are given in the Tables 2–4.

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Results and Discussion

The new ternary compounds with Th_2Zn_{17}-type structure are represented by their cell volumes in Figure 1 together with the cell volumes of the binary rare earth zinc compounds with this structure type reported earlier.[13] It can be seen that generally the cell volumes decrease in agreement with the well-known lanthanoid contraction. Small deviations from the linear decrease may be assigned to small differences in the compositions. A notable exception is the cell volume of the binary compound Yb_2Zn_{17}, where the ytterbium atoms may at least partially be divalent. Another exception, occurring for $Ce_2Ni_3Zn_{14}$, may be rationalized by the presence of mixed or intermediate $Ce^{3+/4+}$ valency. The relative cell volume of this cerium nickel compound is smaller than the cell volumes of the corresponding iron and cobalt compounds $Ce_2Fe_3Zn_{14}$ and $Ce_2Co_3Zn_{14}$. This may be due to the differences of the electronegativities of the late transition elements Fe, Co, and Ni in these compounds. Of these, the nickel atoms are the most noble ones, the ones with the smallest electropositivity, or in other words the ones with the highest electronegativity and the relatively highest electron-drawing power, thus resulting in the highest valency for the cerium atoms in the three compounds $Ce_2Fe_3Zn_{14}$, $Ce_2Co_3Zn_{14}$, and $Ce_2Ni_3Zn_{14}$.

The fifty ternary compounds reported here crystallize with an ordered version of the binary Th_2Zn_{17}-type structure.[8] This structure has already been reported for the binary rare earth zinc compounds Ln_2Zn_{17} with Ln = La–Nd, Sm, and Gd–Lu. Most of these binary compounds Ln_2Zn_{17} are dimorphic, crystallizing also with the closely related (primitive) hexagonal Th_2Ni_{17}-type structure.[10,13–16] The two structures are stacking variants of each other with the same hexagonal lattice constant a, and the lattice constant c of the Th_2Ni_{17}-type structure being two-thirds of the corresponding lattice constant of the Th_2Zn_{17}-type structure. There are certain significant differences in the X-ray powder patterns of the two structure types: the *hkl* reflections 024 and 205 are relatively strong in the powder patterns of the Th_2Zn_{17}-type compounds, and at the corresponding scattering angles the Th_2Ni_{17}-type phases have no strong reflections. On the other hand, the relatively strong reflection 213 of the Th_2Ni_{17}-type compounds has no counterpart for the compounds with Th_2Zn_{17}-type structure. We have paid attention to these differences of the powder patterns to make sure that the assignment of the Th_2Ni_{17}-type structure is correct for the ternary compounds reported here. They were all prepared with an excess of zinc. It seems possible that the Th_2Ni_{17}-type structure might be observed also for the ternary compositions using other preparation conditions.

In an earlier publication on Th_2Zn_{17}-type compounds,[11] it has been noted that the c/a ratio of these hexagonal cells are remarkably similar. We have listed the c/a ratios of the new ternary compounds with this

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Table 4. Interatomic Distances in the Compounds $Ln_2T_3Zn_{14}$ with the Compositions $Gd_2Co_3Zn_{14}$, $Ce_2Rh_{1.90(2)}Zn_{15.10(2)}$, $Pr_2Ni_3Zn_{14}$, and $Sm_2Pd_{1.92(1)}Zn_{15.08(1)}$ and the Binary La_2Zn_{17-x}[a]

		$Gd_2Co_3Zn_{14}$	$Ce_2Rh_{1.90(2)}Zn_{15.10(2)}$	$Pr_2Ni_3Zn_{14}$	$Sm_2Pd_{1.92(1)}Zn_{15.08(1)}$	$La_2Zn_{16.06(6)}$
Ln:	1Zn3	302.5	313.3	309.6	312.8	317.3
	6Zn2 or 6Zn2/T	314.6	321.8	318.5	318.4	325.1
	3Zn1 or 3Zn1/T	320.9	326.2	324.4	322.6	326.4
	3Zn1 or 3Zn1/T	325.4	334.7	329.5	335.8	339.8
	3T or 3T/Zn or 3Zn4	338.8	346.7	343.1	345.0	347.2
	3Zn1 or 3Zn1/T	345.9	350.7	348.7	347.1	350.0
T or T/Zn or Zn4:	4Zn2 or 4Zn2/T	254.7	260.0	257.4	259.6	261.0
	4Zn1 or 4Zn1/T	256.4	262.3	258.3	262.8	266.7
	2Zn3	268.6	275.0	271.8	274.1	278.7
	2Ln	338.8	346.7	343.1	345.0	347.2
Zn1 or Zn1/T:	2T or 2T/Zn or 2Zn4	256.4	262.3	258.3	259.2	266.7
	2Zn1 or 2Zn1/T	260.1	263.6	263.0	262.8	260.7
	2Zn2 or 2Zn2/T	268.7	275.9	273.2	272.6	277.4
	2Zn2 or 2Zn2/T	271.5	276.7	273.7	276.4	279.1
	1Zn3 or 1Zn3/T	274.2	282.1	276.7	284.3	290.1
	1Ln	320.9	326.2	324.5	322.6	326.4
	1Ln	325.4	334.7	329.5	335.8	339.8
	1Ln	345.9	350.7	348.7	347.1	350.0
	1Zn1 or 1Zn1/T	394.1	404.3	400.3	403.3	407.9
Zn2 or Zn2/T:	2T or 2T/Zn or 2Zn4	254.7	260.0	257.4	259.6	261.0
	2Zn2 or 2Zn2/T	260.9	264.9	261.8	267.2	265.8
	2Zn1 or 2Zn1/T	268.7	275.9	273.2	272.6	277.4
	2Zn1 or 2Zn1/T	271.5	276.7	273.7	276.4	279.1
	2Zn3 or 2Zn3/T	294.2	297.7	294.7	299.1	296.3
	2Ln	314.6	321.8	318.5	318.4	325.1
	1Zn2 or 1Zn2/T	365.3	375.4	371.9	367.0	380.9
Zn3 or Zn3/T:	3T or 3T/Zn or 3Zn4	268.6	275.0	271.8	274.1	278.7
	1Zn3 or 1Zn3/T	271.8	271.7	270.7	268.8	262.1
	3Zn1 or 3Zn1/T	274.2	282.1	276.7	284.3	290.1
	6Zn2 or 6Zn2/T	294.2	297.7	294.7	299.0	296.3
	1Ln	302.5	313.3	309.6	312.8	317.3

[a] These distances were calculated with the lattice constants of Table 1. All distances shorter than 420 pm are listed. The standard deviations are all 0.1 pm or less than that.

structure in Table 1. It can be seen that this is also the case for the presently reported compounds. For these, the c/a ratio varies between the value 1.4617 for $La_2Fe_3Zn_{14}$ (and $Sm_2Rh_{3-x}Zn_{14+x}$) and the value 1.4762 for $Ce_2Co_3Zn_{14}$, a difference of only 1.0%.

The structure of the hexagonal compounds $Ln_2Co_3Zn_{14}$ is shown in Figure 3 with that of $Gd_2Co_3Zn_{14}$ as an example. The structure may be viewed as consisting of layers of two kinds, although chemical bonding within and between the layers is of comparable strength. The layers of the type *A* contain all of the cobalt atoms and the zinc atoms Zn1 and Zn3. The layers of the type *B* contain all of the gadolinium atoms and the Zn2 atoms. These layers are flat, whereas the layers of the type *A* are puckered in such a way that the cobalt atoms have three zinc atoms above and three zinc atoms below the projection direction, thus forming a very compressed octahedron. The layers *A* contain relatively large voids *V*1 which are discussed below. If these voids were filled by cobalt atoms, the ratio of cobalt-to-zinc atoms would correspond to Co:Zn = 1:2. Such layers have recently been singled out in structures of ternary rare earth transition metal compounds with a high content of aluminum and gallium, for example, in the structure of $Er_4Pt_9Al_{24}$[17] and in the $Y_2Co_3Ga_9$-type structure[18] of $Dy_2Ru_3Ga_9$.[19] Accounting for the voids, the layers *A* in the structure of $Gd_2Co_3Zn_{14}$ have a Co:Zn ratio of 3:8

and a unit mesh content of Co_3Zn_8, while the composition of the layers *B* is at the ratio Gd:Zn = 1:3 with a mesh content of Gd_2Zn_6. The layers alternate in the sequence *ABA′B′, ABA′B′*, resulting in the formula $Gd_2Zn_6 \cdot Co_3Zn_8 = Gd_2Co_3Zn_{14}$.

Figure 3 also shows the coordination polyhedra in the structure of $Gd_2Co_3Zn_{14}$. All atoms have high coordination numbers (CN), as is typical for intermetallics. The largest atoms are the Gd atoms with the high CN of 19 (3 Co and 16 Zn neighbors). They have the site symmetry 3m with the 3-fold axis going through the Zn3 atom. In the drawing of this coordination polyhedron (Figure 3) the third Co and two of the Zn1 atoms are on the backside and not (Co) or barely (Zn1) visible. The Co atoms have elongated icosahedral coordination (CN 12) with two Gd and ten Zn neighbors. The Zn1 and the Zn2 atoms may also be considered to have a CN of 12, not counting the zinc neighbors at the rather large distances of 394.1 and 365.3 pm, respectively. However, their coordination polyhedra are more distorted. In contrast, the Zn3 atoms have CN 14. All of the three different zinc atoms have gadolinium and cobalt neighbors in addition to the zinc neighbors. The Zn−Zn distances cover the range between 260.1 and 294.2 pm. The weighted average Zn−Zn distances reflect the different CNs with 267.8 pm for Zn1 (CN 12), 273.8 pm for Zn2 (CN 12), and 286.0 pm for Zn3 (CN 14).

Our structure determinations of the ternary compounds with ordered Th_2Zn_{17}-type structure from single-crystal data show that the late transition elements T occupy exclusively the 9d position of this rhombohedral structure. Hence, the ideal composition is $Ln_2T_3Zn_{14}$. This composition was found by us (within the error

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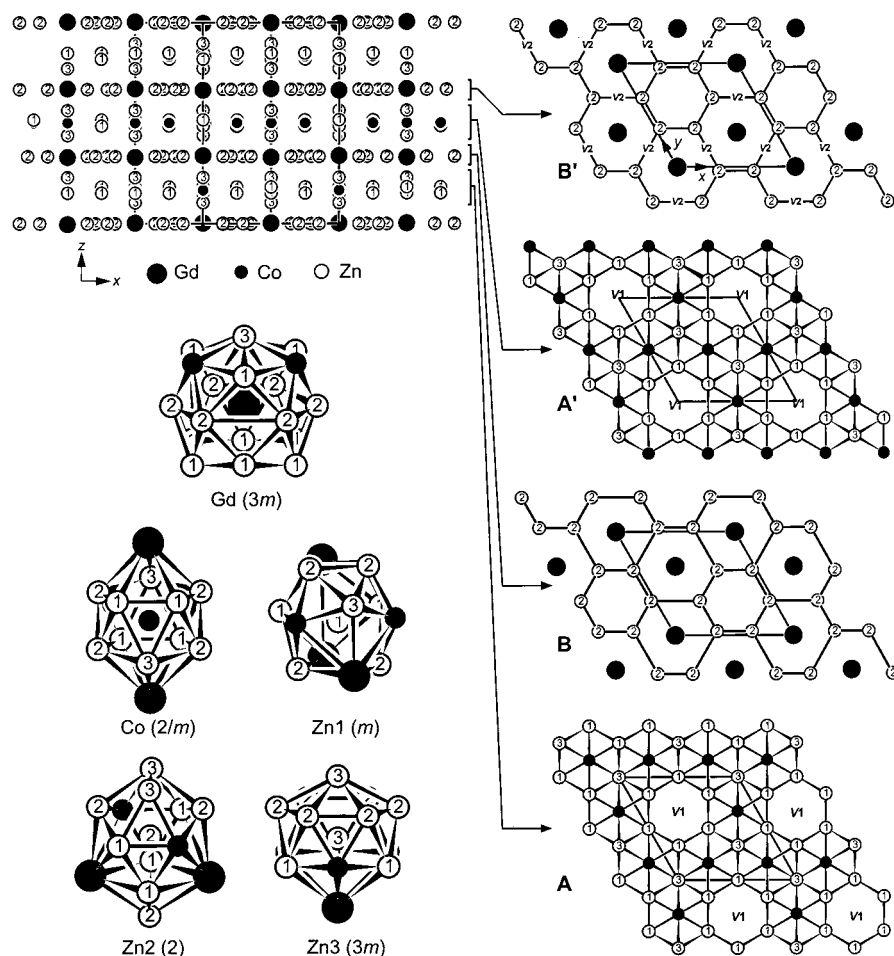
Figure 3. Crystal structure and coordination polyhedra of $Gd_2Co_3Zn_{14}$. In the upper left-hand corner of the figure, the structure is projected perpendicular to the hexagonal axis. Four atomic layers of this projection are (somewhat arbitrarily) singled out and shown in projections along the hexagonal axis on the right-hand side of the figure. The coordination polyhedra of the five atomic sites are shown in the lower left-hand side and the site symmetries of the central atoms are indicated in parentheses. The structure contains relatively large voids $V1$. In the ternary carbides $Ln_2T_{17}C_3$ with $Pr_2Mn_{17}C_{3-x}$-type structure the carbon atoms occupy octahedral voids $V2$ formed by four Zn and two Ln atoms. The positions $V2$ of these carbon atoms are shown in the layer on the upper right-hand corner of the figure.

limits, as discussed below) from the structure refinements of $Gd_2Co_3Zn_{14}$ and $Pr_2Ni_3Zn_{14}$, while a mixed occupancy T/Zn was clearly observed for the 9d position for the compounds $Ce_2Rh_{1.90(2)}Zn_{15.10(2)}$ and $Sm_2Pd_{1.92(1)}$-$Zn_{15.08(1)}$. One of these ternary compounds, $\approx Ce_2Ni_2Zn_{15}$, had already been reported.[20] In that publication it was assumed that the nickel atoms occupy the 6c position. The scattering powers of nickel (atomic number 28) and zinc (30) differ by only 7%. Thus, high-quality X-ray data are needed to distinguish these elements. Our structure determinations clearly show the occupancy of the 9d positions by the transition metal atoms T. However, in the case of $Gd_2Co_3Zn_{14}$ and $Pr_2Ni_3Zn_{14}$ we cannot rule out a mixed T/Zn occupancy for the 9d site at the magnitude as observed for $Ce_2Rh_{1.90(2)}Zn_{15.10(2)}$ and Sm_2-$Pd_{1.92(1)}Zn_{15.08(1)}$. On the other hand, the position 6c, assumed to be occupied by the nickel atoms in Ce_2Ni_2-Zn_{15}, has always been found to be fully occupied by zinc atoms in the present investigation.

The reason for the deviations from the ideal composition $Ln_2T_3Zn_{14}$ in the case of $Ce_2Rh_{1.90(2)}Zn_{15.10(2)}$ and $Sm_2Pd_{1.92(1)}Zn_{15.08(1)}$ is not clear. It could be that the

nonstoichiometric compositions are more stable because their electron count is optimized. In that case the compounds with iron, cobalt, and nickel might also be nonstoichiometric. However, it could also be that the atomic sizes are important. The 9d site of the Th_2Zn_{17}-type structure has the lowest coordination number, and therefore it is well-suited for the small transition metal atoms iron (with the metallic radius[21] for the coordination number 12 of 127.4 pm), cobalt (125.2 pm), and nickel (124.6 pm), whereas the radii for the elements rhodium (134.5 pm), palladium (137.6 pm), and platinum (138.7 pm) are greater and more comparable to the radius of zinc (139.4 pm). In any case, since we have no hard evidence for the iron-, cobalt-, and nickel-containing compounds to be nonstoichiometric, we have used the ideal formulas for these compounds.

Our structure refinement of the binary compound La_2-Zn_{17} showed deviations from the ideal occupancies for the Zn1 and Zn4 sites with occupancies of 89.2(8) and 90.4(8)% corresponding to the composition $La_2Zn_{16.06(6)}$.

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It seems possible that the compound has a homogeneity range. Hence, we cannot rule out the ideal composition. In a previous structure refinement of this compound all atomic positions were refined assuming the ideal composition.[13] The thermal parameters resulting from that investigation do not give any indication for deviations from the ideal occupancies, and there is agreement between the two structure refinements concerning the positional parameters which all agree within 10 standard deviations.

Some ternary rare earth iron carbides $Ln_2Fe_{17}C_{3-x}$ and nitrides $Ln_2Fe_{17}N_{3-x}$ have become important hard magnetic materials.[5,6] The metal positions of these compounds correspond to those of the binary Th_2Zn_{17}-type structure while the carbon and nitrogen atoms occupy the carbon positions of the $Pr_2Mn_{17}C_{3-x}$-type structure.[22,23] Some of these positions are designated with the abbreviation V2 (void 2) in the layer B' in the upper right-hand corner of Figure 3. We thought about the possibility that the binary compounds Ln_2Zn_{17} might be stabilized by the presence of small interstitial atoms such as oxygen or nitrogen, and this was the reason for us to refine the structure of La_2Zn_{17}. A well-known example of such an impurity stabilization by interstitial oxygen is the structure of β-tungsten. This "modification" of tungsten has never been obtained without interstitial impurities. Only 6 at. % oxygen is needed to stabilize this structure, corresponding to the formula $W_3O_{0.2}$.[24] Other well-known examples of impurity stabilization are the many compounds with "filled" Mn_5Si_3 (Mo_5Si_3C- or Hf_5CuSn_3-type structure).[25-28] The final difference Fourier synthesis of the least-squares refinement of the structure of La_2Zn_{17} shows a residual electron density of 1.36 e/Å^3 at the origin of the cell. For the sites corresponding to the carbon position of $Pr_2Mn_{17}C_{3-x}$ (at $x = {}^1/_2$, $y = 0$, $z = 0$) we found an electron density of <0.48 e/Å^3. For an interstitial site, fully occupied by oxygen or nitrogen atoms, according to our experience an electron density of ca. 15 e/Å^3 could be expected. Thus, we can exclude the hypothesis of

Table 5. Positional Parameters and Near-Neighbor Coordinations (pm) of the Vacant Sites V1 and V2 in the Structure of $Gd_2Co_3Zn_{14}$

	$R\bar{3}m$	x	y	z
V1	3a	$^1/_3$	$^2/_3$	$^1/_6$
V2	9e	$^1/_2$	0	0

V1:			V2:		
2Gd	211.6			2Zn2	182.7
6Zn1	257.8			2Zn1	197.1
				2Gd	256.2

impurity stabilization for these binary compounds Ln_2Zn_{17}. Similarly, our refinements of the crystal structures of the compounds $Gd_2Co_3Zn_{14}$, $Ce_2Rh_{1.90(2)}Zn_{15.10(2)}$, $Pr_2Ni_3Zn_{14}$, and $Sm_2Pd_{1.92(1)}Zn_{15.08(1)}$ do not show any significant electron densities at these interstitial sites of the type $V2$.

In addition to the unoccupied site $V2$, the Th_2Zn_{17}-type structure has an even larger unoccupied site, designated as $V1$ (void 1). In Figure 3 these voids are shown on the right-hand side in the layers of the type A. The positions of the voids $V1$ and $V2$ and the distances to the surrounding neighbors are listed in Table 5. As already discussed above, there are no significant electron densities at the positions of these voids in the binary and ternary compounds characterized here. It has been suggested that such voids in compounds with a high content of zinc might contain nonbonding electrons using orbitals of the zinc atoms,[2,29-32] and this may also be the case for the binary compounds with Th_2Zn_{17}-type structure and the ternary compounds with ordered Th_2Zn_{17}-type structure reported here.

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