

Isothermal sections of the Sm–Co–Zn and Gd–Co–Zn phase diagrams at 470 K

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Phase equilibria in the Sm–Co–Zn and Gd–Co–Zn ternary systems have been investigated by X-ray powder diffraction. The isothermal sections of their phase diagrams have been constructed over the whole concentration range at 470 K. The Sm–Co–Zn system is characterized by the formation of six ternary compounds: $\text{Sm}_2\text{Co}_2\text{Zn}_{15}$, $\text{SmCo}_{3.2-3.5}\text{Zn}_{1.8-1.5}$, $\text{SmCo}_{4.4}\text{Zn}_{0.6}$, $\text{Sm}_2\text{Co}_5\text{Zn}_2$, SmCo_2Zn , and $\text{SmCo}_2\text{Zn}_{20}$. The Gd–Co–Zn system is described by the formation of four ternary compounds: $\text{Gd}_2\text{Co}_2\text{Zn}_{15}$, $\text{GdCo}_{3.5-3.8}\text{Zn}_{1.5-1.2}$, $\text{Gd}_2\text{Co}_5\text{Zn}_2$, and $\text{GdCo}_2\text{Zn}_{20}$. The maximum solid solubility of Zn at 470 K is observed in the binary SmCo_2 compound (15 at.%), and the maximum solid solubility of Co is observed in the GdZn compound (10 at.%). The homogeneity ranges of the solid solutions on the basis of the other binary phases do not exceed 5 at.%.

Ternary alloy system / Phase diagram / Intermetallic compound / Solid Solution

1. Introduction

In the last few decades, alloys of rare-earth (*R*) and 3*d* transition metals (*M*) have received much attention because of their interesting crystal structures, promising physical properties, and potential applications as, for example, magnetic materials [1,2] and hydrogen storage devices [3,4]. Despite this interest, many of these systems remain poorly understood and their phase diagrams undetermined, including those containing zinc as the third component. The present work is devoted to the study of ternary *R–M–Zn* systems (in particular, with *R* = Sm, Gd; *M* = Co), the isothermal sections of their phase diagrams, and the crystal structures and homogeneity ranges of new ternary compounds and solid solutions.

Previously, we reported the isothermal sections of the La–Co–Zn, Ce–Co–Zn and Tb–Co–Zn systems at 470 K [5–7]. These systems are characterized by the formation of a series of isotypic ternary compounds, among which are rhombohedral $R_2\text{Co}_2\text{Zn}_{15}$ (str. type $\text{Ce}_2\text{Al}_2\text{Co}_{15}$) and $R_2\text{Co}_5\text{Zn}_2$ (str. type $\text{Ce}_2\text{Ni}_5\text{Zn}_2$), hexagonal $R\text{Co}_2\text{Zn}$ (str. type YRh_2Si), and cubic $R\text{Co}_{5-x}\text{Zn}_x$ (str. type AuBe_5) phases. In addition, $R_3\text{Co}_{1-x}\text{Zn}_x$ (str. type AuCu_3), $\text{CeCo}_{2.1-2.6}\text{Zn}_{2.9-2.4}$ (str. type CaCu_5), and several previously unknown compounds were found in the systems containing La and Ce. Later, we determined the crystal structures of the unknown phases and reported them as $R\text{CoZn}_2$ (str. type ErCuCd_2 , space group *Cmcm*) [8] and

$\text{LaCo}_{2.17}\text{Zn}_{0.83}$ (str. type PrCo_2Ga , space group *Pmma*) [9]. Solid solutions based on binary phases are formed in these systems along isoconcentrates of rare-earth element because Co and Zn are easily substituted for each other.

The study of other *R–Co–Zn* systems remains limited to specific compositions and structures, namely $R\text{Co}_2\text{Zn}_{20}$ (*R* = Sc, Y, and the later rare-earth elements Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu) with cubic $\text{CeCr}_2\text{Al}_{20}$ -type structure [10], $R(\text{CoZn})_7$ (*R* = Tb) with hexagonal TbCu_7 -type structure [11], and $R_2\text{Co}_3\text{Zn}_{14}$ (*R* = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm) with rhombohedral $\text{Th}_2\text{Zn}_{17}$ -type structure [12]. The possibility of formation and stability of these phases in the investigated ternary {Sm, Gd}–Co–Zn systems at 470 K will be discussed herein.

2. Experimental

The ternary systems Sm–Co–Zn and Gd–Co–Zn were studied through the analysis of 85 and 82 binary and ternary alloys, respectively. The samples, each with a total mass of about 1 g, were synthesized by arc melting of the elemental metals (all with nominal purity better than 99.9 wt.%) under purified argon atmosphere at a pressure of 50 kPa. To achieve homogenization, the alloys were sealed in silica ampoules under vacuum and annealed at 470 K for 1500 h. Finally they were quenched in cold water. The compositions of the samples were determined by

the comparison of the mass of each obtained alloy with the mass of the initial batch. Energy-dispersive X-ray analysis was carried out on a LEITZ-AMR 1600T electron microscope in cases where an accurate determination of the composition was deemed necessary.

X-ray powder diffraction was the main method used for the phase analysis of the samples. Powder patterns were obtained at room temperature from finely ground samples using powder diffractometers DRON-2.0 (FeK α -radiation, 2°/min scan speed) and PHILIPS X'Pert Pro (CuK α -radiation, 20° ≤ 2θ ≤ 100°, 0.02° scan step, 8-10 s/point scan speed). Pure silicon was added to the samples as an internal standard to achieve better accuracy in 2θ values. For phase identification, experimental powder patterns were compared with those calculated for pure components and known binary and ternary compounds by the program Powder Cell [13]. The observed diffraction intensities were indexed using TREOR-90 [14], and the lattice parameters were refined by the least-squares method using LATCON [15] and DBW-3.2s programs [16].

3. Results and Discussion

3.1. Binary systems

The binary systems Sm–Co, Sm–Zn, Gd–Co, Gd–Zn and Co–Zn that delineate the investigated ternary systems have been extensively studied previously, although there remains some discrepancy in the number, composition, and thermal stability of the reported binary phases [17,18]. Under the conditions of our experiment, we have confirmed the existence of the binary phases shown in Fig. 1 and Fig. 2. For those compounds that can undergo polymorphic transitions, the following modifications were found to be thermodynamically stable at the annealing temperature: rhombohedral Sm₂Co₁₇ and Gd₂Co₁₇ (Th₂Zn₁₇-type), rhombohedral Sm₂Co₇ (Gd₂Co₇-type), hexagonal Gd₂Co₇ (Ce₂Ni₇-type), hexagonal Sm₂Zn₁₇ and Gd₂Zn₁₇ (Th₂Ni₁₇-type), orthorhombic SmZn₂ (KHg₂-type), and hexagonal Gd₁₃Zn₅₈ (own type).

3.2. Sm–Co–Zn

The isothermal section of the Sm–Co–Zn phase diagram at 470 K, constructed over the whole concentration range and determined by analysis of 85 alloys, consists of 25 single-phase regions, 52 two-phase regions and 29 three-phase regions (Fig. 1). Some binary Sm–Co and Sm–Zn phases dissolve the third component, forming limited solid solutions along the isoconcentrates of samarium. The maximum solid solubility of Zn was observed in SmCo₂ at 15 at.% (Fig. 3). Smaller solubility of Zn, up to 5 at.%, was detected on the basis of the binary phases Sm₂Co₁₇, Sm₂Co₇, SmCo₃, and Sm₃Co. There is no visible solubility on the basis of other binary phases at the annealing temperature.

Six ternary compounds were observed in the Sm–Co–Zn system at 470 K: SmCo₂Zn₂₀, Sm₂Co₂Zn₁₅, SmCo_{3.2-3.5}Zn_{1.8-1.5}, SmCo_{4.4}Zn_{0.6}, Sm₂Co₅Zn₂, and SmCo₂Zn. All the compounds exhibit a fixed composition, except for SmCo_{3.2-3.5}Zn_{1.8-1.5}, which has a homogeneity range of about 5 at.%. SmCo_{3.2-3.5}Zn_{1.8-1.5} was found to be isotypic with the cubic AuBe₅-type structure, with Sm atoms occupying the Au sites (4a) and a statistical mixture of Co and Zn atoms occupying the Be sites (4c and 16e). Another new compound found at the same content of samarium, SmCo_{4.4}Zn_{0.6}, crystallizes in the hexagonal CaCu₅-type structure, with Sm atoms situated in the Ca sites (1a) and a statistical mixture of Co and Zn atoms in the Cu sites (2c and 3g). Details on the crystal structure and magnetic properties of this compound are described elsewhere [19]. In the Co-rich region of the phase diagram, the two compounds Sm₂Co₅Zn₂ and SmCo₂Zn were observed, which adopt the rhombohedral Ce₂Ni₅Zn₂-type and hexagonal YRh₂Si-type structures, respectively. The distribution of atoms in both structures remains the same as in the parent structure types. The Zn-rich phase SmCo₂Zn₂₀ was confirmed to crystallize with the cubic CeCr₂Al₂₀-type structure [10]. Another ternary compound found in this region, Sm₂Co₂Zn₁₅, belongs to the rhombohedral Ce₂Al₂Co₁₅-type structure, which is an ordered variant of the Th₂Zn₁₇-type structure. The distribution of atoms in this structure is the same as previously found by single-crystal X-ray diffraction for La₂Ni₂Zn₁₅ [20] and Tb₂Co₂Zn₁₅ [21]. Recently, Gross *et al.* reported a similar series of compounds, however with slightly different composition, R₂Co₃Zn₁₄ (R = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er), and at higher temperature, 770 K [12]. According to their data, Co occupies the 9d position in this structure, whereas our results show that Co is in the 6c position. Because Zn and Co have similar scattering factors and atomic radii, they cannot be easily distinguished by X-ray diffraction alone and other methods may be useful in resolving their exact distribution. Table 1 lists crystallographic data for all the Sm–Co–Zn compounds found here, together with published data for the confirmed ones.

3.3. Gd–Co–Zn

The isothermal section of the Gd–Co–Zn phase diagram at 470 K, constructed over the whole concentration range and determined by analysis of 82 alloys, consists of 25 single-phase regions, 51 two-phase regions and 27 three-phase regions (Fig. 2). Analogous to Sm–Co and Sm–Zn, binary compounds of the Gd–Co and Gd–Zn systems can dissolve the third component forming solid solutions along the isoconcentrates of gadolinium. The largest solubility of Co, up to 10 at.%, is observed in the GdZn compound (Fig. 4). The solubility of Zn in Gd–Co alloys is less significant and reaches 5 at.% in Gd₂Co₇ and GdCo₂. The remaining binary phases do not have noticeable homogeneity ranges at the annealing temperature.

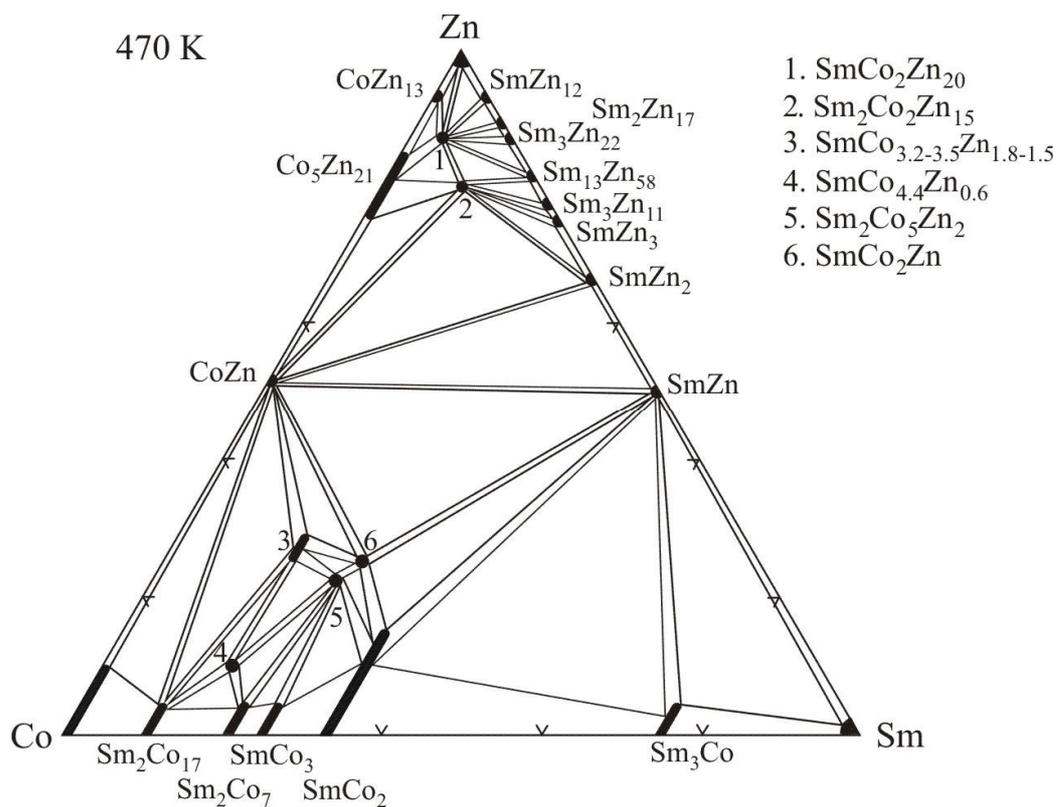


Fig. 1 Isothermal section of the Sm–Co–Zn phase diagram at 470 K.

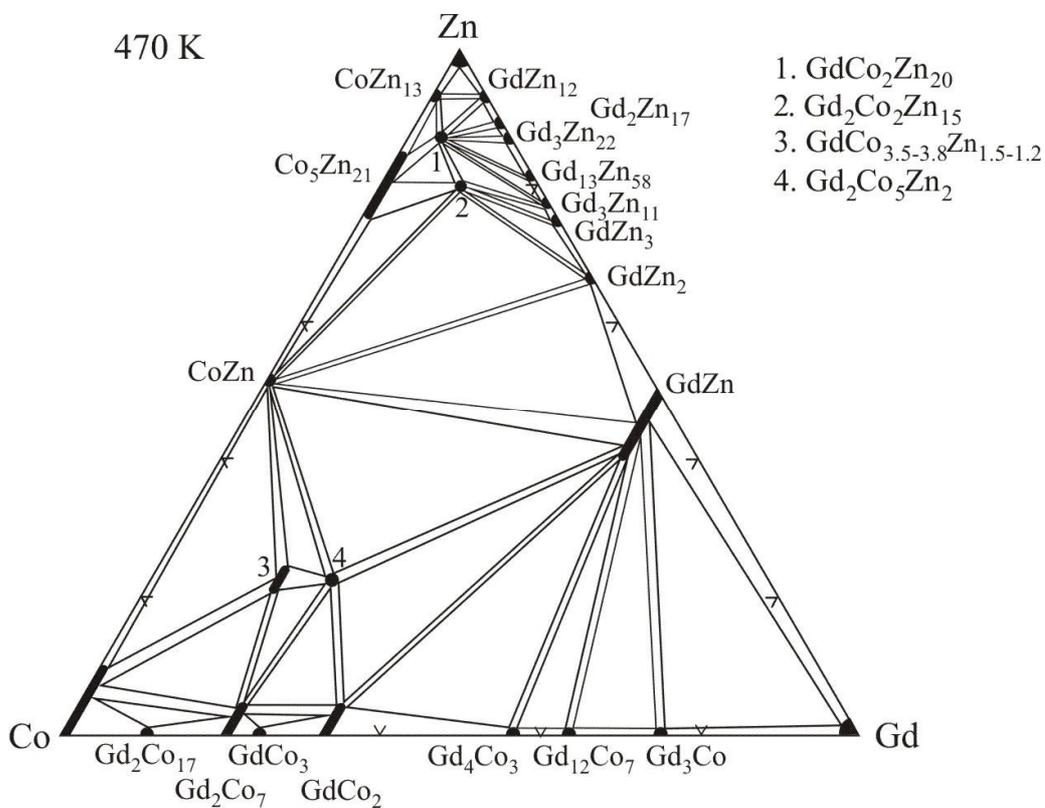
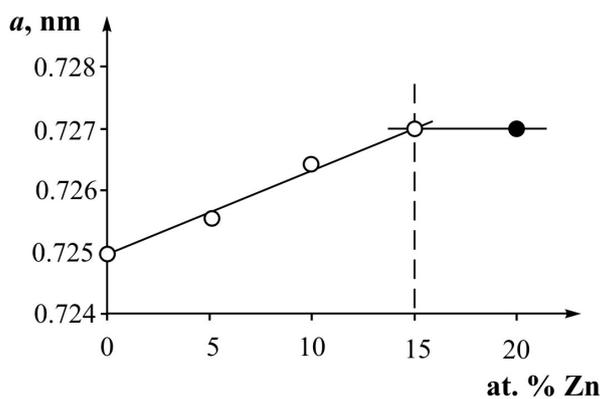
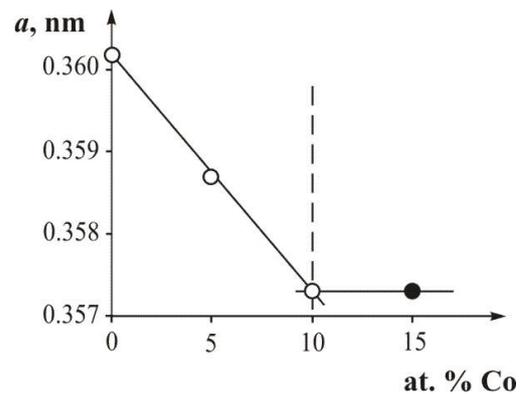


Fig. 2 Isothermal section of the Gd–Co–Zn phase diagram at 470 K.

Table 1 Ternary compounds of the Sm–Co–Zn and Gd–Co–Zn ternary systems.

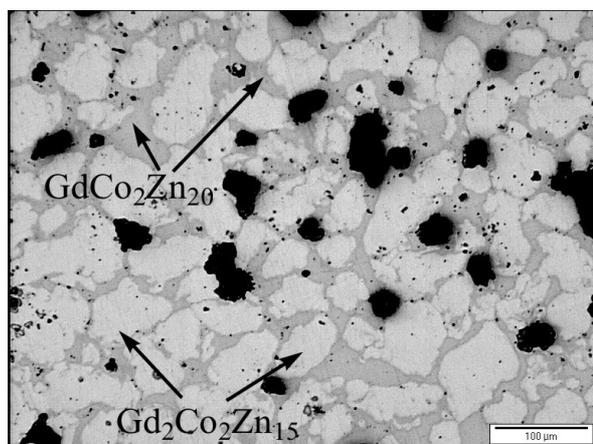
Compound	Structure type	Space group	Pearson code	Lattice parameters, nm		Reference
				<i>a</i>	<i>c</i>	
SmCo ₂ Zn ₂₀	CeCr ₂ Al ₂₀	<i>Fd</i> 3 <i>m</i>	<i>cF</i> 184	1.4082(1)	–	[6]
				1.4046(2)	–	this work
Sm ₂ Co ₂ Zn ₁₅	Ce ₂ Al ₂ Co ₁₅	<i>R</i> 3̄ <i>m</i>	<i>hR</i> 57	0.8983(3)	1.3213(6)	this work
				0.8933(2)	1.3165(3)	[8]
SmCo _{3.2-3.5} Zn _{1.8-1.5}	AuBe ₅	<i>F</i> 4̄3 <i>m</i>	<i>cF</i> 24	0.7259(3)÷0.7221(3)	–	this work
SmCo _{4.4} Zn _{0.6}	CaCu ₅	<i>P</i> 6/ <i>mmm</i>	<i>hP</i> 6	0.5002(1)	0.3972(1)	this work
Sm ₂ Co ₅ Zn ₂	Ce ₂ Ni ₅ Zn ₂	<i>R</i> 3̄ <i>m</i>	<i>hR</i> 54	0.5009(2)	3.665(1)	this work
SmCo ₂ Zn	YRh ₂ Si	<i>P</i> 6 ₃ / <i>mmc</i>	<i>hP</i> 24	0.5134(1)	1.6632(6)	this work
GdCo ₂ Zn ₂₀	CeCr ₂ Al ₂₀	<i>Fd</i> 3̄ <i>m</i>	<i>cF</i> 184	1.4060(1)	–	[6]
				1.4014(2)	–	this work
Gd ₂ Co ₂ Zn ₁₅	Ce ₂ Al ₂ Co ₁₅	<i>R</i> 3̄ <i>m</i>	<i>hR</i> 57	0.8987(1)	1.3169(6)	this work
				0.8907(3)	1.3095(5)	[8]
GdCo _{3.5-3.8} Zn _{1.5-1.2}	AuBe ₅	<i>F</i> 4̄3 <i>m</i>	<i>cF</i> 24	0.7189(3)÷0.7143(2)	–	this work
Gd ₂ Co ₅ Zn ₂	Ce ₂ Ni ₅ Zn ₂	<i>R</i> 3̄ <i>m</i>	<i>hR</i> 54	0.5008(3)	3.634(4)	this work

**Fig. 3** The change of lattice parameter *a*, nm, for the SmCo_{2-x}Zn_x solid solution.**Fig. 4** The change of lattice parameter *a*, nm, for the GdZn_{1-x}Co_x solid solution.

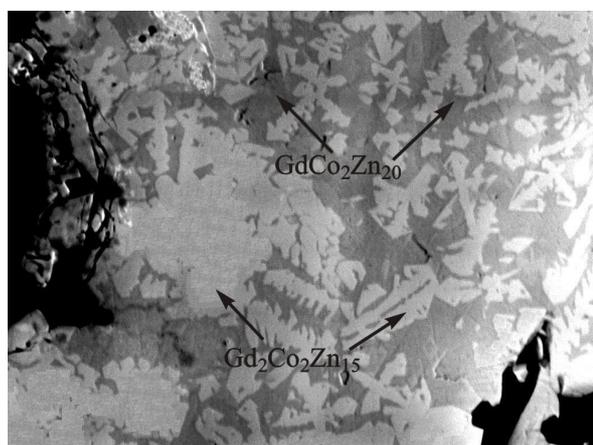
Four ternary compounds were found in the Gd–Co–Zn system at 470 K: GdCo₂Zn₂₀, Gd₂Co₂Zn₁₅, GdCo_{3.5-3.8}Zn_{1.5-1.2}, and Gd₂Co₅Zn₂. The compound GdCo_{3.5-3.8}Zn_{1.5-1.2} has a homogeneity range of about 5 at.%, whereas the remaining compounds are formed at essentially fixed concentration of the components. The crystal structure of GdCo_{3.5-3.8}Zn_{1.5-1.2} belongs to

the cubic AuBe₅-type structure. As in the isotypic compound with samarium, the Gd atoms are situated in the Au sites (4*a*) and a statistical mixture of Co and Zn atoms in the Be sites (4*c* and 16*e*). There is only one more compound observed in the Co-rich region of the phase diagram. It adopts the rhombohedral Ce₂Ni₅Zn₂-type structure and can be described by the

formula $\text{Gd}_2\text{Co}_5\text{Zn}_2$. The Zn-rich region of the phase diagram is characterized by the formation of two compounds: $\text{Gd}_2\text{Co}_2\text{Zn}_{15}$, which crystallizes in the rhombohedral $\text{Ce}_2\text{Al}_2\text{Co}_{15}$ -type structure, and $\text{GdCo}_2\text{Zn}_{20}$, which was confirmed to belong to the cubic $\text{CeCr}_2\text{Al}_{20}$ -type structure [10]. The compositions of both compounds were confirmed by EDX of the two-phase $\text{Gd}_8\text{Co}_{10}\text{Zn}_{82}$ alloy (Fig. 5). The obtained Gd:Co:Zn ratios of 4.97:8.10:85.99 for the darker phase and 10.38:10.52:79.31 for the lighter phase correspond perfectly to the compositions expected from the structure (1:2:20 and 2:2:15). The results of Gross *et al.* [12] at 770 K lead again to the composition $\text{Gd}_2\text{Co}_3\text{Zn}_{14}$. Table 1 lists crystallographic data for all ternary compounds found in the Gd–Co–Zn system at 470 K.



(a)



(b)

Fig. 5 Optical (a) and electron (b) microscopy photographs of the $\text{Gd}_8\text{Co}_{10}\text{Zn}_{82}$ alloy.

4. Conclusions

Detailed analysis of the phase equilibria in the Sm–Co–Zn and Gd–Co–Zn systems at 470 K shows

that they are related to each other and to the previously reported R – M –Zn systems ($R = \text{La, Ce, Tb}$; $M = \text{Fe, Co, Ni, Cu}$) [5–7,20,22–25]. In both systems, the formation of solid solutions based on binary compounds along the isoconcentrates of rare earth metals was observed. Solutions based on thermodynamically stable phases like $R\text{Co}_2$ and GdZn , or phases with the same stoichiometry like $R_2\text{Co}_{17}$ and $R_2\text{Zn}_{17}$, or SmCo_3 and SmZn_3 , have the larger homogeneity ranges. The extent of the solid solutions generally decreases upon substitution of R from Sm to Gd, consistent with the pattern identified previously in R – M –Zn systems where the solubility regions of the binary phases diminish with the transition from early to late rare earth.

Most of the ternary compounds are formed along the cross-sections corresponding to the binary compositions of the R – M systems and were found to crystallize in the same structure types as the binary compounds or to be ternary superstructures of them. For example, ternary compounds $R\text{Co}_{5-x}\text{Zn}_x$ based on binary $R\text{M}_5$ are formed along the isoconcentrate 16.67 at.% of R , and one of them, $\text{SmCo}_{4.4}\text{Zn}_{0.6}$, crystallizes with the same CaCu_5 -type structure as binary phases. In a similar manner, the compounds $R_2\text{Co}_2\text{Zn}_{15}$ (str. type $\text{Ce}_2\text{Al}_2\text{Co}_{15}$) are superstructures of the binary phases $R_2\text{M}_{17}$ (str. type $\text{Th}_2\text{Zn}_{17}$), $R_2\text{Co}_5\text{Zn}_2$ (str. type $\text{Ce}_2\text{Ni}_5\text{Zn}_2$) to $R_2\text{Co}_7$ (str. type Gd_2Co_7), and $R\text{Co}_2\text{Zn}$ (str. type YRh_2Si) to $R\text{Co}_3$ (str. type CeNi_3). Previous studies and our work confirm that ternary compounds with the composition $R\text{M}_2\text{Zn}_{20}$ ($\text{CeCo}_2\text{Al}_{20}$ -type structure) exist only in the systems containing late rare-earth elements.

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