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Peculiarities of the composition and structure of the compounds of the rare-earth–Ni–In systems

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Abstract

Data on the composition and structure of 117 ternary compounds of the rare-earth metals, nickel and indium were generalized. Relations between the structure, the metric parameters of the unit cell and valence state of the atoms were considered. © 1997 Elsevier Science S.A.

Keywords: Intermetallic compound; Crystal structure; Indium; Nickel; Rare-earth

1. Introduction.

In recent years ternary intermetallic compounds of indium, rare-earths (R) and transitions metals have attracted attention from researchers. Many of these compounds have interesting physical properties. The greatest number of such compounds have been found in the R–Ni–In systems. The first ternary indides of Ni and a rare-earth with equiatomic composition were synthesized and investigated by Ferro et al. [1]. Later we found new compounds and described their crystal structure during a study of isothermal sections of the phase diagrams of the R–Ni–In systems [2–19].

The aim of the present work is a generalization of the data and a search for the peculiarities of the composition and crystal structure of the compounds of the R–Ni–In systems.

2. Experimental details

The alloys were prepared by melting compact metals of high purity in an electrical arc furnace under Ar atmosphere. The investigation of the crystal structure of the compound was carried out by the powder method (diffractometers DRON-2.0, DRON-3M, DRON-4.07, HZG-4a) and the single crystal method (autodiffractometers Syntex P1, Syntex $P2_1$, DARCH-1, KM-4). The package of programs CSD [20] was used for solving the structure of the compounds.

3. Results and discussion

Data for the 117 ternary compounds of the R–Ni–In systems for which the crystal structure has been determined are listed in Table 1. In spite of the incomplete data on the investigation of the isothermal sections it is possible to conclude that the elements of the cerium subgroup form more compounds than do those of the yttrium subgroup. The region of the existence of the above indicated compounds is between 8.3 and 63.2 at.% R and between 5.3 and 66.7 at.% In. The lowest R content for the formation of the compounds in R–Cu–In is equal to 7.1 at.% and 7.7 at.% (compounds with the $NaZn_{13}$ [21] and $ThMn_{12}$ [22] type structure, respectively) and to 14.3 at.% in the R–Co–In systems (compounds with the $HoCoGa_5$ [23] type structure). Minimum R content for the formation of the compounds in the R–{Co,Ni,Cu}–In systems decreases at the transition from Co to Cu. In the case of $Pr_2Ni_{16}In$ [$= Pr_2(Ni,In)_{17}$], the stabilization by indium of the Th_2Ni_{17} structure which is absent in the Pr–Ni system is observed. The compounds with this type of

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Table 1
Distribution of the compounds in the rare-earth–Ni–In systems on their structure types

No.	Compounds	R at.%	Structure type	Pearson code	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
1	RNi_9In_2	8.3	YNi_9In_2	tP24	+	+	+	+	+	+	+	+	+	+	+	−	−	−	+
2	RNi_3In_6	10.0	$LaNi_3In_6$	oP20	+	+	+	+	−	+	−	−	−	−	−	−	−	−	−
3	$R_2Ni_{16.0}In_{1.0}$	10.5	Th_2Ni_{17}	hP38	−	−	+	−	−	−	−	−	−	−	−	−	−	−	−
4	RNi_5In	14.3	$CeNi_5Sn$	hP28	+	+	+	+	+	+	−	−	−	−	−	−	−	−	−
5	RNi_4In	16.7	$MgCu_4Sn$	cF24	−	+	+	+	+	−	+	+	+	+	+	+	+	+	+
6	RNi_3In_2	16.7	$HoNi_{2.6}Ga_{2.4}$	hP18	+	−	+	−	−	−	−	−	−	−	−	−	−	−	−
7	$RNiIn_4$	16.7	$YNiAl_4$	oC24	+	+	+	+	−	+	−	−	−	−	−	−	+	−	−
8	$R_4Ni_7In_8$	21.1	$Ce_4Ni_7In_8$	oC76	+	+	+	+	+	−	−	−	−	−	−	−	−	−	−
9	$R_5Ni_6In_{11}$	22.7	$Pr_5Ni_6In_{11}$	oC44	+	+	+	+	−	−	−	−	−	−	−	−	−	−	−
10	RNi_2In	25.0	$PrCo_2Ga$	oP8	+	−	+	+	−	−	−	−	−	-	−	−	−	−	−
11	$RNiIn_2$	25.0	$MgCuAl_2$	oC16	−	−	−	−	−	+	+	+	+	−	−	−	−	−	+
12	$R_{10}Ni_9In_{20}$	25.6	$Ho_{10}Ni_9In_{20}$	tP78	−	−	−	−	−	−	−	−	−	+	+	+	−	+	−
13	$RNiIn$	33.3	$ZrNiAl$	hP9	+	+	+	+	⊕	−	⊕	⊕	⊕	⊕	⊕	⊕	−	⊕	⊕
14	$R(Ni,In)_2$	33.3	AlB_2	hP3	⊕	⊕	⊕	⊕	⊕	+	−	−	−	−	−	−	−	−	−
15	R_2Ni_2In	40.0	Mn_2AlB_2	oC10	−	−	−		+	−	+	+	+	+	+	+	−	+	+
16	R_2Ni_2In	40.0	Mo_2FeB_2	tP10	+	+	+	+	−	−	−	−	−	−	−	−	−	−	−
17	$R_2Ni_{2-x}In$ $(x = 0.22)$	42.0	Mo_2FeB_2	tP10	−	−	−	−	+	−	+	+	+	+	+	+	−	+	+
18	$R_5Ni_2In_4$	45.5	$Lu_5Ni_2In_4$	oP22	−	−	−	−	−	−	−	−	−	+	+	+	−	+	−
19	$R_{12}Ni_6In$	63.2	$Sm_{12}Ni_6In$	cI38	+	−	+	+	+	−	+	−	−	−	−	−	−	−	+

+, the compound exists; ⊕, the compound has region of homogeneity; −, the compound has not been found.

structure exist in the binary R–Ni systems (R ≡ Nd ÷ Lu, Y). The R–Ni–In systems are characterized by a lower number of compounds compared to the R–Ni–Ga systems [24] in which, due to the smaller difference between the atom sizes of Ni and Ga, the solid solutions on the base of the binary compounds are formed and many ternary compounds have a homogeneity range along the constant content of rare-earth metal. The formation of the solid solutions on the base of binary compounds and homogeneity ranges for the ternary compounds are not characteristic of the R–Ni–In systems. The compounds with the AlB_2 type structure (extension 5 at.%) and ZrNiAl [17], which are on the 33.3 at.% R section, are the exception.

It is necessary to indicate that the AlB_2-type compounds only exist with the light rare-earth metals (La, Ce, Pr, Nd, Sm, Eu) and that the compounds of these rare-earths with the ZrNiAl type structure have a constant composition (compound EuNiIn has still not been found). If a compound with the AlB_2 type structure is not formed, then a compound with a ZrNiAl type structure (R ≡ Y, Gd, Tb, Dy, Ho, Er, Tm, Lu) has a significant homogeneity range from RNiIn composition in the direction of the increase of the In content up to composition $RNi_{1-x}In_{1+x}$, where x has an average value of 0.4. Samarium in this case has an intermediate position; both its compounds have homogeneity ranges. Within the homogeneity range the substitution of Ni by In is always accompanied by an increase in the volume of the cell. This observation is consistent with the size of the Ni atom ($r_{In} > r_{Ni}$), however, both lattice parameters do not increase in all cases.

The investigated ternary compounds crystallize in 18 structure types, among which seven have new structure types. The $MgCu_4Sn$, YNi_9In_2, ZrNiAl and Mo_2FeB_2 types have the complete series of the isostructural compounds. But the compounds of samarium and R of the yttrium subgroup, which crystallize in the Mo_2FeB_2 type, have the small defect of Ni and the $R_2Ni_{2-x}In$ composition ($x \sim 0.22$). The $LaNi_3In_6$, $CeNi_5Sn$, $YNiAl_4$, $Ce_4Ni_7In_8$, $Pr_5Ni_6In_{11}$, AlB_2 and $Sm_{12}Ni_6In$ structure types are characteristic of compounds with R from the cerium subgroup, and $Ho_{10}Ni_9In_{20}$, Mn_2AlB_2 and $Lu_5Ni_2In_4$ structure types are characteristic of compounds with R from the yttrium subgroup. Most compounds of the R–Ni–In systems are related to the binary compounds. They can be superstructures to them, contain their fragments or be the members of the homological series which are based on more simple types (Table 2).

The structure types in which the compounds of the R–Ni–In systems crystallize (except the types Th_2Ni_{17}, $Ho_9Ni_9In_{20}$ and $Sm_{12}Ni_6In$ with large unit cells) can be divided into three groups. The first one contains the compounds with the large Ni content (YNi_9In_2, $CeNi_5Sn$ and $MgCu_4Sn$ structure types). These compounds have four layers altering in the shortest direction which is equal to ~0.5 nm. Cubic structure $MgCu_4Sn$ when presented in hexagonal aspect, in

Table 2
Relations between the structures in the rare-earth–Ni–In systems

I. Superstructure		Structure
YNi_9In_2	→	$Ce(Ni_{0.45}Mn_{0.55})_{11}$
$MgCu_4Sn$	→	$AuBe_5 \rightarrow MgCu_2$
$MgCuAl_2$	→	$PuBr_3$
$ZrNiAl$	→	Fe_2P
Mo_2FeB_2	→	U_3Si_2
II. Structure		**Fragments**
YNi_9In_2	=	$CeMg_2Si_2 + Zr_4Al_3$
$LaNi_3In_6$	=	$MgCuAl_2$ + 'Ni_2In_4'
$CeNi_5Sn$	=	$CaCu_5$ + '$CeNi_2In$' + Ni_3In
$Ce_4Ni_7In_8$	=	$CeMg_2Si_2 + AuCu_3 + CsCl + HoNi_{2.6}Ga_{2.4}$
$Pr_5Ni_6In_{11}$	=	$CeMg_2Si_2 + AuCu_3 + CsCl + CaCu_5$
$PrCo_2Ga$	=	$CsCl + CaCu_5$
Mo_2FeB_2	=	$CsCl + AlB_2$
Mn_2AlB_2	=	$CsCl + AlB_2$
$Lu_5Ni_2In_4$	=	$CsCl + AlB_2$

case of $CeNi_4In$ has $a \approx 0.5$ nm, $c \approx 1.22$ nm. The second group ($LaNi_3In_6$, $Ce_4Ni_7In_8$, $Pr_5Ni_6In_{11}$, $YNiAl_4$ and $MgCuAl_2$ structure types) contains the compounds with a bigger In content; they have two layers in the shortest direction equal to ~ 0.45 nm. It is possible to include the compounds with the $PrCo_2Ga$ type structure into this group, which has a lower In content, but has two layers with the shortest lattice parameter of ~ 0.45 nm. The compounds with the average R content (ZrNiAl, AlB_2, Mo_2FeB_2, Mn_2AlB_2 and $Lu_5Ni_2In_4$ structure types), which are similar to those of the second group have two layers and form the third group. But the shortest period of these compounds is less than one (~ 0.4 nm) in spite of a larger R content.

The compounds of the first group are characteristic of high values of coordination number (CN) of all atoms, which slowly decrease in the direction of the second and third group. If coordination polyhedra of the smallest atoms (Ni) for a compound of the first group are icosahedra (or their defect derivatives) then for the compounds of the second and the third group they are trigonal prisms with three or four additional atoms. The CN of the In atoms changes in the same way and for the compounds of the second group coordination polyhedra are only deformed cubo-octahedra (CN = 12).

It was underlined that at the transition from the second to third group of the compounds in spite of increasing the rare-earth content, which has a bigger atom size than In or Ni, the decreasing of the shortest period observed; the RNiAl (ZrNiAl structure type) [24] compounds isostructural with the respective indium compounds having smaller volume of the unit cell were characterized by a bigger value of the shortest period. Analogously, the R_2Ni_2Al and R_2Ni_2Ga compounds (Mo_2NiB_2 structure type) [24] have also bigger values of the shortest lattice parameter than those relative to the R_2Ni_2In compounds (Mo_2FeB_2 and Mn_2AlB_2 structure type). In spite of the fact that the last compounds are not isostructural in our opinion, such a comparison is correct because in all cases the unit cell contains 10 atoms (4R + 4Ni + 2X) (Fig. 1). Analogous disparity of the shortest lattice parameter is characteristic of RCuIn and RCuAl with the structure type ZrNiAl. For the compounds rich in X component (for example $YNiAl_4$) for all known compounds of indium, all the lattice parameters are bigger than those of the relevant Al or Ga compounds [24].

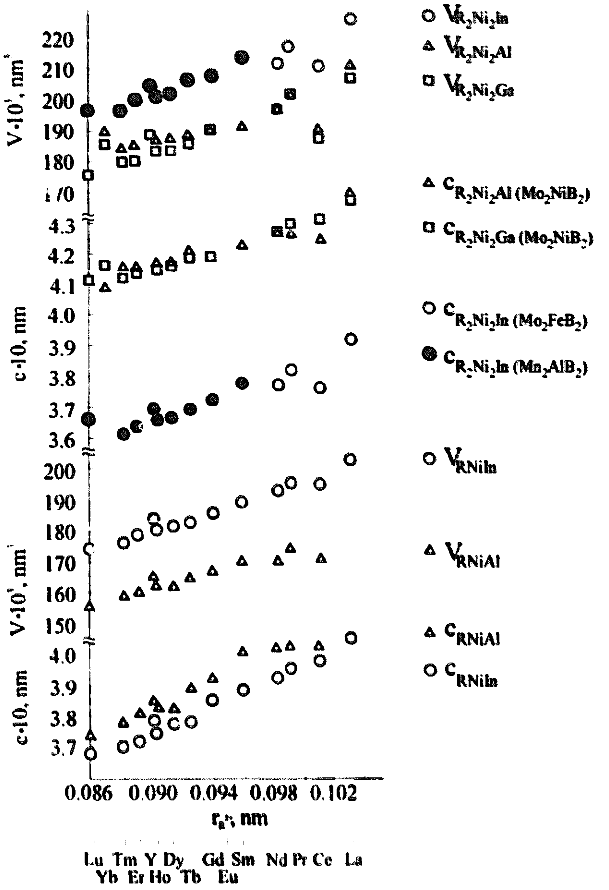

Fig. 1. Change of the volume and the shortest c period for some indides, gallides and aluminides depending on size of R^{3+} ions.

Indicated disparity can be explained by the strong polarization of the In atoms; spheroids having a value of the small semiaxis less than radius Al or Ga atom lie on the plane perpendicular to the shortest period and as a result the value of this period for indides is smaller than for that in the aluminides or gallides. The analogous polarization of In atoms is obviously characteristic of the compound with the AlB_2 and $Lu_5Ni_2In_4$-types. From this it is possible to explain

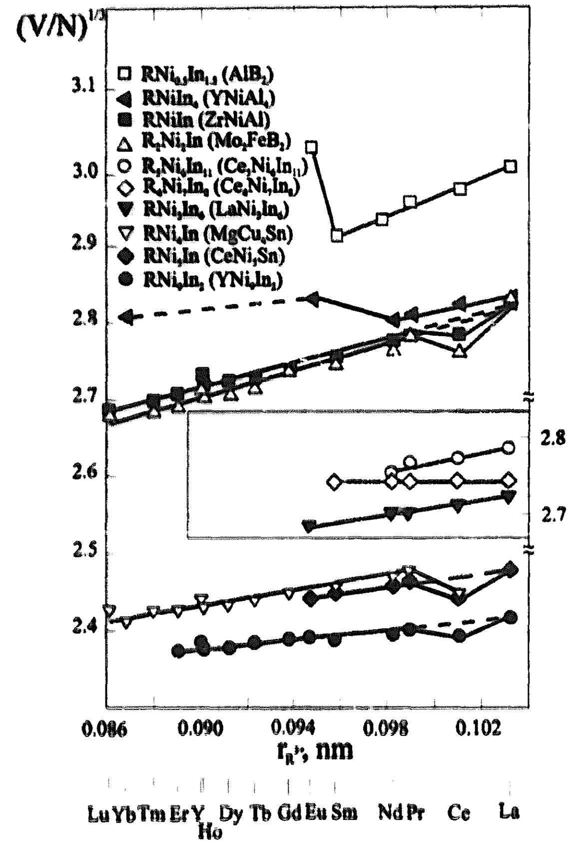

Fig. 2. Dependence of the linear parameter $(V/N)^{1/3}$ (V is a volume of the unit cell, N is a number of atoms per unit cell) on size of R^{3+} ion.

the existence of antibatic, in some cases, change of periods within the homogeneity range of the compounds with the ZrNiAl or AlB_2 type structure.

Change of the linear parameter $(V/N)^{1/3}$ (where V is a volume of the unit cell, N is a number of atoms per unit cell) depending on the size of the R^{3+} ion, according to Shannon [25] for the series of the isostructural compounds are shown in Fig. 2. This change confirms with the effect of the lanthanide contraction. It is seen that for the Ni-rich compounds of cerium, a negative deviation from the linearity was observed. This shows the intermediate valence state, or valence equal to four for $CeNi_9In_2$, $CeNi_5In$, $CeNi_4In$, CeNiIn and Ce_2Ni_2In. It was confirmed by the experimental investigation that in $CeNi_9In_2$ there is Ce^{+4} [26], in Ce_2Ni_2In, according to Gordon et al. [32], Ce is in valence state + 4, according to Kaczorowski et al. [33] it is in intermediate valence state as well as in CeNiIn [29–31]. According to Pöttgen [27], in $CeNiIn_4$ there is Ce^{+3}: the same was reported for $Ce_5Ni_6In_{11}$ [28]. The Ni-rich compounds of Eu and Yb contain these elements in the valence state of + 3, and In-rich compounds contain Eu and Yb in the valence state of less than + 3 ($EuNiIn_4$, $YbNiIn_4$, $Eu(Ni,In)_2$, $EuNiIn_2$). The investigations of the $EuNiIn_4$ compound show that in this compound Eu is in a valence state of + 2 [34].

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