



Ternary system Er–Ni–In at $T=870$ K

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ABSTRACT

Isothermal section of the Er–Ni–In system at $T=870$ K was constructed by means of X-ray powder diffraction and EDX-analyses. Nine ternary compounds, namely ErNi_9In_2 (Y Ni_9In_2 -type), $\text{Er}_{1-1.22}\text{Ni}_4\text{In}_{1-0.78}$ (MgCu $_4$ Sn-type), $\text{Er}_{10}\text{Ni}_{9.07}\text{In}_{20}$ (Ho $_{10}\text{Ni}_9\text{In}_{20}$ -type), $\text{ErNi}_{1-0.60}\text{In}_{1-1.40}$ (ZrNiAl-type), $\text{Er}_2\text{Ni}_2\text{In}$ (Mn $_2\text{AlB}_2$ -type), $\text{Er}_2\text{Ni}_{1.78}\text{In}$ (Mo $_2\text{FeB}_2$ -type), $\text{Er}_5\text{Ni}_2\text{In}_4$ (Lu $_5\text{Ni}_2\text{In}_4$ -type), $\text{Er}_5\text{Ni}_2\text{In}$ (Mo $_5\text{SiB}_2$ -type), and $\text{Er}_{13.53}\text{Ni}_{3.14}\text{In}_{3.33}$ (Lu $_{14}\text{Co}_2\text{In}_3$ -type), exist in the Er–Ni–In system at this temperature. The substitution of Ni for In was observed for $\text{ErNi}_{1-0.60}\text{In}_{1-1.40}$ and In for Er in the case of related compounds ErNi_2 and ErNi_4In . Er can enter NiIn (CoSn-type) leading to including-substitution type of compound $\text{Er}_{0-0.12}\text{NiIn}_{1-0.89}$. Basic magnetic properties of the $\text{Er}_{0.04}\text{NiIn}_{0.97}$, ErNi_2 , $\text{Er}_{0.9}\text{Ni}_2\text{In}_{0.1}$, and ErNi_4In phases were inspected. Electrical-resistivity studies were performed on the ErNiIn , $\text{ErNi}_{0.9}\text{In}_{1.1}$, and ErNi_4In phases.

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1. Introduction

A general effort to extend our knowledge of materials with various characteristics led us to exploration of metallic systems including ternary rare earth systems with *d*-metals and *p*-elements, which exhibit a large richness of phases [1]. This is true also for the R–Ni–In systems, where various crystal structures of ternary compounds have been determined. The isothermal sections of the phase diagram Ce–Ni–In have been constructed [2] and crystal structures of about 130 ternary indides have been identified in this and related systems [3,4].

The subject of the present work is the investigation of components interaction in the Er–Ni–In ternary system. A complete isothermal section in the full concentration range at $T=870$ K has been constructed, with the focus on phases existing over a certain homogeneity regions. Selected compounds were briefly characterized as to their magnetic properties. Some preliminary results were presented in Ref. [5].

The temperature of investigation was chosen to correspond a state, which can be easily obtained by annealing. In general, the annealing temperature must be as high as possible for the fast achieving a homogenization; on the other hand, the samples must be in solid state. The annealing temperatures for majority of investigated ternary systems R–*d*-metals–X (R–rare earth, X–Si, Ge, Al, Ga, and In) are in the 770–1070 K range. For the case of

indides, the annealing temperature $T=870$ K is quite favourable and has been used in many cases [1].

The binary systems Er–Ni [6], Ni–In [7–9], and Er–In [10], which are around the investigated ternary system, were studied in quite some detail. The phase diagrams of these systems have been constructed and crystal structures of binary compounds determined. Concerning the phase diagram of the Ni–In binary system, the small differences in homogeneity regions and melting temperatures of binary compounds exist in the literature. The Er–Ni, Ni–In, and Er–In binary systems are characterized by complicated interaction of components. The rather large number of binary compounds form in all these systems: 11 binary compounds exist in the Er–Ni system, 8—in the Ni–In system, and 5—in the Er–In system. In addition, a limited solubility of In in Er and Ni exist in the Er–In and Ni–In binary systems, and only Er_5In_3 , $\text{Ni}_{13}\text{In}_9$, phases ζ , and δ form homogeneity regions.

2. Experimental

Starting materials for the preparation of the alloys were ingots of the erbium and nickel, and indium tear drops, all with nominal purities better than 99.9%. 73 ternary and two binary samples (of a typical mass of 1–2 g) were synthesized by melting the pure elements in an arc-furnace on a water-cooled Cu-plate under an argon atmosphere (sponge Ti was used as a getter). The buttons were turned over and remelted two times to ensure homogeneity. The weight losses were smaller than 1% in all cases. The alloys were subsequently sealed in evacuated silica tubes and annealed at $T=870$ K for 720 h and quenched in cold water without

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breaking the tubes. Chemical and phase compositions of samples are shown in Fig. 1.

Investigation of the isothermal sections of Er–Ni–In ternary systems was carried out by X-ray powder diffraction method. The X-ray phase analysis was performed using film data (Debye–Scherrer technique, RKD-57.3 camera, Cr–K-radiation) and powder diffractometers (DRON-2.0, Fe–K α -radiation, Ge as an internal standard; Seifert XRD7, Cu–K α -radiation).

The indexing of the obtained diffraction data of the ternary alloys was performed by comparison with calculated data (the program Powder Cell [11]). The lattice parameters of some phases were calculated using the program LATCON [12]. In selected cases the composition of some samples was analyzed in a scanning electron microscope (LEICA 420i) by means of electron microprobe analysis using ErF₃, Ni, and InAs as standards.

Magnetic measurements were performed in the temperature range 2–300 K in magnetic field up to 6 T by means of extraction magnetometer (Quantum Design PPMS) in the form of powder sample with randomly oriented grains fixed by a glue. The electrical resistivity was measured by four-probe method in the temperature range 80–380 K for ErNi_{0.9}In_{1.1} and ErNiIn phases and 4–300 K for the ErNi₄In compound.

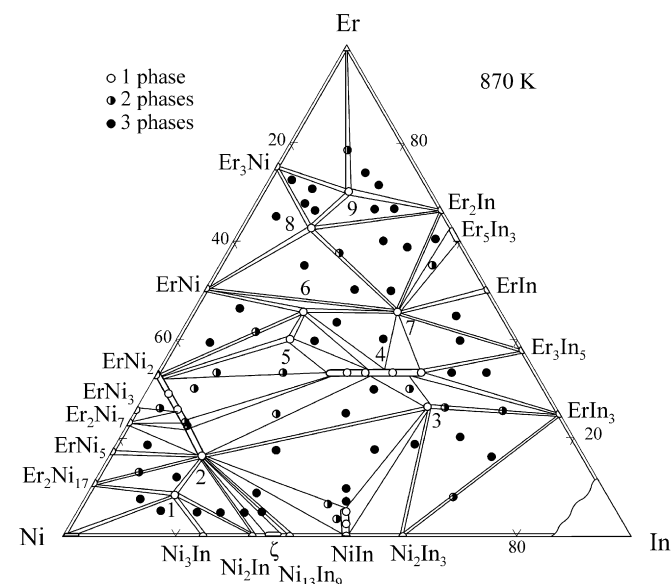


Fig. 1. Chemical and phase composition of samples and isothermal section of the Er–Ni–In system at $T=870$ K.

Table 1
Crystallographic characteristics of ternary compounds in the Er–Ni–In system.

No.	Compound	Structure type	Space group	Lattice parameters (nm)			Refs.
				<i>a</i>	<i>b</i>	<i>c</i>	
1	ErNi ₉ In ₂	YNi ₉ In ₂	<i>P4/mbm</i>	0.8190	–	0.4801	[28]
2	ErNi ₄ In	MgCu ₄ Sn	<i>F43m</i>	0.6996	–	–	[29]
	Er _{1–1.22} Ni ₄ In _{1–0.78}			0.6993–0.7017	–	–	[17]
	Er ₁₀ Ni _{9.07} In ₂₀	Ho ₁₀ Ni ₉ In ₂₀	<i>P4/nmm</i>	1.3250	–	0.9070	[30]
3				1.3230	–	0.9052	[31]
				1.3254	–	0.9064	[32]
				0.7441	–	0.3723	[33]
				0.7412–0.7656	–	0.3739–0.3693	[13–15]
				0.3893	1.4110	0.3639	[34]
4	ErNiIn	ZrNiAl	<i>P6̄2m</i>	0.7310	–	0.3654	[35]
5	Er ₂ Ni ₂ In	Mn ₂ AlB ₂	<i>Cmmm</i>	0.7386	–	0.3614	[36]
	Er ₂ Ni _{1.78} In	Mo ₂ FeB ₂	<i>P4/mbm</i>	0.7386	–	0.3614	[36]
6	Er _{2.30} Ni _{1.84} In _{0.70}	Er _{2.3} Ni _{1.84} In _{0.7}	<i>P4/m</i>	1.7722	0.7866	0.3558	[37]
	Er ₅ Ni ₂ In ₄	Lu ₅ Ni ₂ In ₄	<i>Pbam</i>	1.7722	0.7866	0.3558	[37]
7	Er ₅ Ni ₂ In	Mo ₅ SiB ₂	<i>I4/mcm</i>	0.7546	–	1.3169	[38]
8	Er _{13.53} Ni _{3.14} In _{3.33}	Lu ₁₄ Co ₂ In ₃	<i>P42/nmc</i>	0.9442	–	2.2691	[39]

3. Results

3.1. The phase analysis of Er–Ni–In ternary system

The isothermal section of Er–Ni–In ternary system at $T=870$ K is shown in Fig. 1. It was confirmed that at 870 K the following binary compounds exist: Er₂In (Ni₂In-type), Er₅In₃ (Mn₅Si₃-type), ErIn (CsCl-type), Er₃In₅ (Pu₃Pd₅-type), ErIn₃ (AuCu₃-type); Er₃Ni (Fe₃C-type), ErNi (FeB-type), ErNi₂ (MgCu₂-type), ErNi₃ (NbBe₃-type), Er₂Ni₇ (Gd₂Co₇-type), ErNi₅ (CaCu₅-type), Er₂Ni₁₇ (Th₂Ni₁₇-type); Ni₃In (Ni₃Sn-type), Ni₂In (Ni₂In-type), phase ζ (Ni_xIn_{1–x}, NiAs-type), Ni₁₃In₉ (Ni₁₃Ga₉-type), NiIn (CoSn-type), phase δ (Ni_xIn_{1–x}, CsCl-type), and Ni₂In₃ (Ni₂Al₃-type). Almost none of the binary compounds dissolve the third component. The exception is the existence of solid solutions based on NiIn and ErNi₂ binary compounds.

The phase equilibrium of Er–Ni–In system at 870 K is characterized by the formation of nine ternary compounds with crystallographic parameters given in Table 1. Rodewald et al. [36] reported on existence of Er_{2.30}Ni_{1.84}In_{0.70}. The authors succeeded to extract a single crystal of it from arc-melted sample and determined that the Er_{2.30}Ni_{1.84}In_{0.70} compound crystallizes with a new superstructure upon the Mo₂FeB₂ type. We did not find this compound in samples annealed at 870 K. Instead Er₂Ni₂In (Mn₂AlB₂-type) [34] and Er₂Ni_{1.78}In (Mo₂FeB₂-type) [35] were indicated in the present study. The reason of the discrepancy may be in the fact that Er_{2.30}Ni_{1.84}In_{0.70} may be thermodynamically stable only at higher temperatures.

3.2. ErNi_{1–0.60}In_{1–1.40} ternary compound

The ternary compound ErNiIn crystallizes in the ZrNiAl structure type. The homogeneity region was determined for this compound across the section 33.3 at% Er [13]. Variations of lattice parameters of some samples revealed that the homogeneity region extends from 33.3 to 46.6 at% In (Fig. 2a) and the composition of compound is described by the formula ErNi_{1–0.60}In_{1–1.40}. The volume and the lattice parameter *a* increase (*c* decreases) in the homogeneity range of ErNi_{1–0.60}In_{1–1.40} due to the substitution of smaller atoms of Ni by larger atoms of In.

Gondek et al. [14] and Tyvanchuk et al. [15] reported on magnetic properties of this compound. The magnetic behaviour changes from ferromagnetic for equiatomic composition ($T_C=9$ K) to antiferromagnetic (with similar ordering temperatures) for non-stoichiometric one with increase in indium content. Two samples of ErNiIn and ErNi_{0.9}In_{1.1} were chosen for the electrical resistivity study (Fig. 3). The values of resistivity at $T=80$ K are

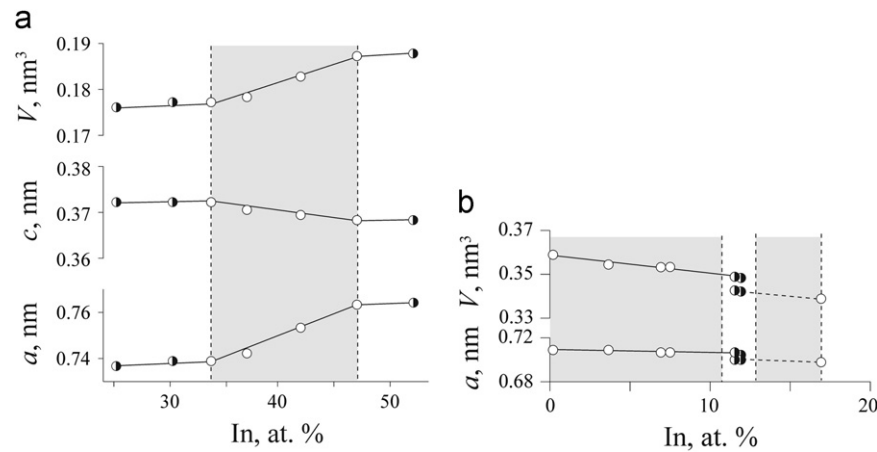


Fig. 2. Dependence of the lattice parameters and the unit cell volume V of $\text{ErNi}_{1-0.60}\text{In}_{1.00-1.40}$ (a), and $\text{Er}_{1-0.68}\text{Ni}_2\text{In}_{0-0.32}$ and $\text{Er}_{1-1.22}\text{Ni}_4\text{In}_{1-0.78}$ compounds (b) vs. the concentration of In.

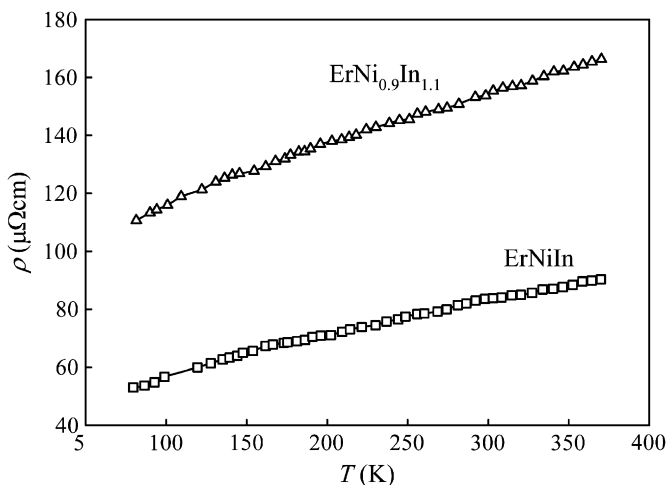


Fig. 3. Temperature dependence of electrical resistivity of ErNiIn and $\text{ErNi}_{0.9}\text{In}_{1.1}$. The absolute accuracy of resistivity values, given by uncertainty of the geometrical factor, is typically better than 10%.

0.53 and $1.11 \mu\Omega\text{m}$ for ErNiIn and $\text{ErNi}_{0.9}\text{In}_{1.1}$, respectively, and they increase almost linearly to $T=300 \text{ K}$ reaching 0.84 and $1.55 \mu\Omega\text{m}$, respectively. The linear increase at high temperatures is typical for electron–phonon scattering [16]. The higher resistivity values for $\text{ErNi}_{0.9}\text{In}_{1.1}$ can be explained by higher atomic disorder, leading to a random potential causing additional temperature independent scattering of conduction electrons [16].

3.3. $\text{Er}_{1-0.68}\text{Ni}_2\text{In}_{0-0.32}$ and $\text{Er}_{1.22-1}\text{Ni}_4\text{In}_{0.78-1}$ phases

The ternary compound ErNi_4In (MgCu_4Sn -type structure, space group $F\bar{4}3m$) is closely related to the Laves phase ErNi_2 (MgCu_2 -type structure, space group $Fd\bar{3}m$). The small difference in size of Er and In atoms and the relation between the structures allow an opposite solubility between these two compounds. Therefore a solid solution based on ErNi_2 and homogeneity region of ErNi_4In ternary compound are along the section 66.7 at% Ni and the composition the phases may be described as $\text{Er}_{1-0.68}\text{Ni}_2\text{In}_{0-0.32}$ and $\text{Er}_{1.22-1}\text{Ni}_4\text{In}_{0.78-1}$ (Fig. 2b). In the phase with MgCu_2 -structure type, the site of Mg atoms (Wyckoff position $8b$) is occupied by a statistical mixture of Er and In atoms. In the case of ternary $\text{Er}_{1.22-1}\text{Ni}_4\text{In}_{0.78-1}$, the substitution of Er atoms by In atoms take place at the $4c$ site [17].

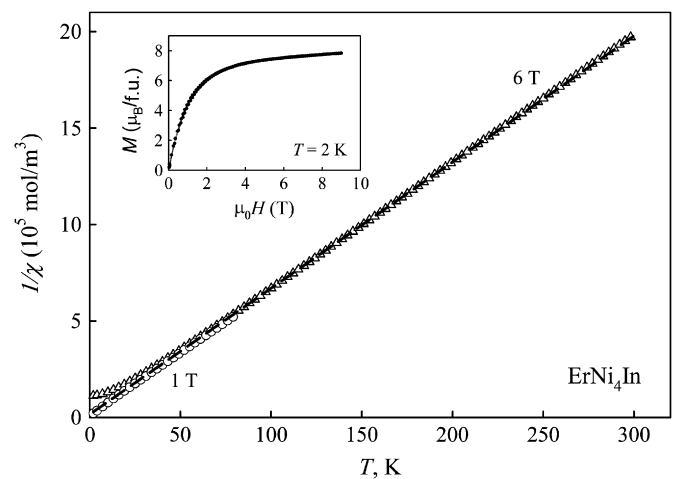


Fig. 4. Temperature dependence of inverse magnetic susceptibility of ErNi_4In in various magnetic fields. The data for $\mu_0H=1 \text{ T}$ (circles) follow the dashed line, representing the fit to the CW law. The data in $\mu_0H=6 \text{ T}$ (triangles) show a saturation at the low- T limit. Its reason is seen in the inset, capturing the field dependence of magnetization of ErNi_4In , measured $T=2 \text{ K}$.

In addition, we measured the magnetic susceptibility of ErNi_4In , which can be compared with the data on ErNi_2 and $\text{Er}_{0.9}\text{Ni}_2\text{In}_{0.1}$ reported in Ref. [17]; results are displayed in Fig. 4. The temperature range applied captures the paramagnetic state with the susceptibility following the Curie–Weiss law. The paramagnetic Curie temperatures Θ_p for ErNi_2 , $\text{Er}_{0.9}\text{Ni}_2\text{In}_{0.1}$, and ErNi_4In phases are 32 K , 24 K , and -2.6 K , respectively. The effective magnetic moments per Er ion for all these compounds are close to the theoretical effective moment of Er^{3+} ions ($9.58 \mu_B$) and are $9.1(1)$, $9.1(2)$ and $9.90(1) \mu_B$. The similar value for ErNi_2 ($9.37 \mu_B$) was reported in Ref. [18]. The saturated magnetization approaches $8 \mu_B/\text{Er atom}$ in this case, i.e. approaching the theoretical value $9.0 \mu_B$. The saturation in high fields (i.e. the non-linearity of the Brillouin function describing the response of magnetization of local moments to magnetic field) causes that the susceptibility in the low-temperature range becomes field dependent.

The temperature-dependent electrical resistivity of ErNi_4In compound (Fig. 5) exhibits a common metallic behaviour without any sign of magnetic order. One can assume an antiferromagnetic ordering at still lower temperatures, as Θ_p is negative and small in absolute value.

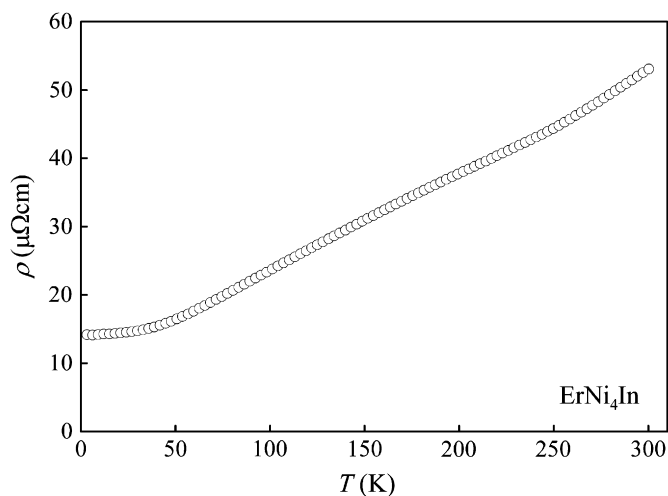


Fig. 5. Temperature dependence of electrical resistivity of ErNi_4In .

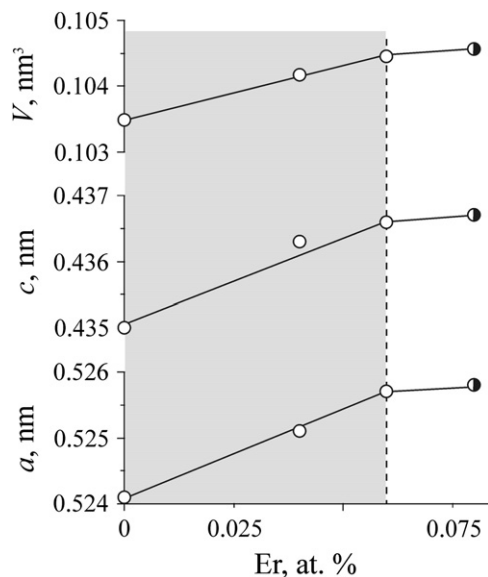


Fig. 6. Dependence of the lattice parameters and unit cell volume V vs. the content of Er in the solid solution based on NiIn.

3.4. $\text{Er}_{0-0.12}\text{NiIn}_{1-0.89}$ solid solution

The solid solution based on NiIn (CoSn-type structure, space group $P6/mmm$) exists in the Er–Ni–In system. The microprobe analysis results of $\text{Er}_{0.02}\text{Ni}_{0.49}\text{In}_{0.49}$, $\text{Er}_{0.04}\text{Ni}_{0.48}\text{In}_{0.48}$, and $\text{Er}_{0.06}\text{Ni}_{0.47}\text{In}_{0.47}$ samples show that they consist of a single-phase. The experimentally determined compositions of these samples were close to the compositions of ingots and can be described as $\text{Er}_{0.02}\text{Ni}_{0.49}\text{In}_{0.49}$, $\text{Er}_{0.05}\text{Ni}_{0.48}\text{In}_{0.47}$, and $\text{Er}_{0.07}\text{Ni}_{0.49}\text{In}_{0.44}$, respectively. In the samples with the composition $\text{Er}_{0.04}\text{Ni}_{0.50}\text{In}_{0.46}$ and $\text{Er}_{0.06}\text{Ni}_{0.50}\text{In}_{0.44}$ we observed the coexistence of the solid solutions based on NiIn and ternary compound ErNi_4In (Fig. 1).

Therefore, the solid solution based on NiIn binary compounds ($a=0.5211$ nm, $c=0.4349$ nm) can be assumed as stable for 0–7 at% Er (Fig. 6). The increase in Er atoms content in the solid solution leads to the increase of lattice parameters (c/a remains approximately 0.83). According to Ref. [19], rather large interstitials exist in the CoSn-type structure, the centre of which are in the $(0\ 0\ 1/2)$ position. Therefore, it was supposed that Er atoms enter this site. For more exact determination of Er atomic positions, the crystal structure of $\text{Er}_{0.02}\text{Ni}_{0.49}\text{In}_{0.49}$ and $\text{Er}_{0.04}\text{Ni}_{0.48}\text{In}_{0.48}$

samples were investigated using X-ray powder diffraction. The scattering density inside the unit cell of NiIn was calculated using the GFourier Program 04.04 for the both samples. It was determined that Er atoms really are located at $(0\ 0\ z)$ with $z \approx 0.43$, which corresponds to the $2e$ Wyckoff site. The subsequent refinement of crystal structure was performed with the FullProf 3.40 program [20]. Crystal data and details of structure refinements are listed in Table 2. Fig. 7 shows the X-ray diffraction patterns of the respective samples [21].

In the NiIn binary compound, the Ni atom is coordinated by 10-vertices consisting of hexagon $4\text{Ni}+2\text{In}(1a)$ and a rectangle of $4\text{In}(2d)$. The six Ni atoms and nine In atoms ($3\text{In}(2d)+6\text{In}(1a)$) form a 15-vertices polyhedron around $\text{In}(2d)$. The coordination polyhedron around $\text{In}(1a)$ is 20-vertices polyhedron consists of $6\text{Ni}+12\text{In}(2d)+2\text{In}(1a)$. The interatomic distances Ni–Ni and Ni– $\text{In}(1a)$ are equal and shortest (0.2622 nm) in this structure. In case of the $\text{Er}_{0-0.12}\text{NiIn}_{1-0.89}$ phase, some changes in coordination sphere take place because of the Er atoms included. The coordination number of some Ni atoms becomes 11. Four Ni, one $\text{In}(1a)$, four $\text{In}(2d)$, and two Er atoms form the coordination sphere of Ni atoms. The coordination polyhedrons of $\text{In}(2d)$ and $\text{In}(1a)$ atoms are still 15- and 20-vertices polyhedrons, respectively, but one Er atom takes the place of one $\text{In}(1a)$ in both coordination polyhedrons. The interatomic distances between Ni and In atoms change slightly. The equal distances Ni–Ni and Ni– $\text{In}(1a)$ stay the shortest in the $\text{Er}_{0-0.12}\text{NiIn}_{1-0.89}$ phase (0.26256 nm). The distances between Ni, In, and Er atoms are given in Fig. 8.

The magnetic susceptibility of $\text{Er}_{0.04}\text{NiIn}_{0.97}$ phase obeys a modified Curie–Weiss law in the whole studied temperature range (Fig. 9), with the paramagnetic Curie temperature $\Theta_p = -11.6$ K and the temperature-independent term $\chi_0 = -4.766 \times 10^{-9}$ m³/mol. Such behaviour can be interpreted as presence of paramagnetic ions in a diamagnetic matrix. The effective magnetic moment $10.2 \mu_B/\text{Er}$ is slightly enhanced with respect to the theoretical value for $4f^{11}$ ($9.58 \mu_B$). Considering the error due to the low Er concentration, this difference is not significant. One should note that a spin polarization of the $5d$ and other electronic states, which can be often as high as $0.5 \mu_B$, can modify the $4f$ magnetic moments of rare-earth atoms in metals. On the other hand, the

Table 2

Results of structure refinements of $\text{Er}_{0.04}\text{NiIn}_{0.97}$ and $\text{Er}_{0.07}\text{NiIn}_{0.94}$ phases.

Sample composition	$\text{Er}_{0.02}\text{Ni}_{0.49}\text{In}_{0.49}$	$\text{Er}_{0.04}\text{Ni}_{0.48}\text{In}_{0.48}$
Calculated composition	$\text{Er}_{0.04}\text{NiIn}_{0.97}$	$\text{Er}_{0.07}\text{NiIn}_{0.94}$
Molar mass (g/mol)	176.76	178.33
Equipment	Seifert XRD7	Seifert XRD7
Wavelength	$\text{CuK}\alpha$ (1.54178)	$\text{CuK}\alpha$ (1.54178)
2θ range for data collection	15.00° – 130.00°	15.00° – 130.00°
Step size in 2θ (deg.)	0.02	0.02
Structure type	CoSn	CoSn
Space group	$P6/mmm$	$P6/mmm$
Lattice parameters (nm)	$a=0.52457(4)$ $c=0.43578(4)$ $V=0.10385(2)$ nm ³	$a=0.52512(5)$ $c=0.43637(4)$ $V=0.10421(2)$ nm ³
Volume		
Er at $2e$ (0 0 z)	$z=0.410(1)$	$z=0.3462(8)$
Occupation	0.065(6)	0.111(1)
B_{iso} (\AA^2)	0.60(1)	1.05(1)
Ni at $3f$ (1/2 0 0)		
Occupation	1.00	1.00
B_{iso} (\AA^2)	0.45(2)	0.59(2)
In1 at $2d$ (1/3 2/3 1/2)		
Occupation	1.00	1.00
B_{iso} (\AA^2)	0.60(1)	1.05(1)
In2 at $1a$ (0 0 0)		
Occupation	0.91(1)	0.831(2)
B_{iso} (\AA^2)	0.60(1)	1.05(1)
R_f (%)	4.25	6.32
R_{Bragg} (%)	5.82	7.28

saturated magnetization at $T=2$ K, which corresponds to only $5.0 \mu_B/\text{Er}$ is considerably lower than the theoretical value $9.0 \mu_B$. The difference can be attributed e.g. to a strong magnetic anisotropy reducing the magnetization of randomly oriented grains.

4. Discussion

The interaction of indium with rare earths and 3d-metals has complex character due to different electron structure of interacting components. The large number of ternary compounds with various structure types exists in R–T–In systems. Almost all

$R_xT_yIn_z$ ternary indides with large Ni content have a complicated multilayer structure with high coordination numbers of all types of atoms. Two-layer structure across the shortest period characterizes the compounds from the central part of the concentration triangle. Compounds with high rare-earth metals content as well as Ni-rich compounds have a complicated structure, but coordination numbers of the atoms are much smaller.

Nine ternary compounds were found to form in the investigated system Er–Ni–In at $T=870$ K. It is less than in the comparable system Ce–Ni–In (13 compounds), the isothermal section of which has been constructed [1,2], and other R–Ni–In systems, which have been partly explored testing the existence of isostructural compounds [1]. The common feature of the R–Ni–In systems is the formation of isostructural compounds RNi_9In_2 (YNi₉In₂-type structure), RNi_4In (MgCu₄Sn-type structure), $RNiIn$ (ZrNiAl-type structure), and compounds with the Mo_2FeB_2 -type structure. The fundamental difference between the Ce–Ni–In and Er–Ni–In systems is in the nature of solid solutions and homogeneity region of the compounds. In the first system, the compound with the Mo_2FeB_2 -type structure is formed at the stoichiometric composition, but in the second case the same type structure is defective on Ni atoms ($Er_2Ni_{1.78}In$). The substitution of Ni for In atoms take place in homogeneity regions of $CeNi_{0.3-0.2}In_{1.7-1.8}$ ternary compounds with the AlB_2 type structure, while no compound with this type structure was found in

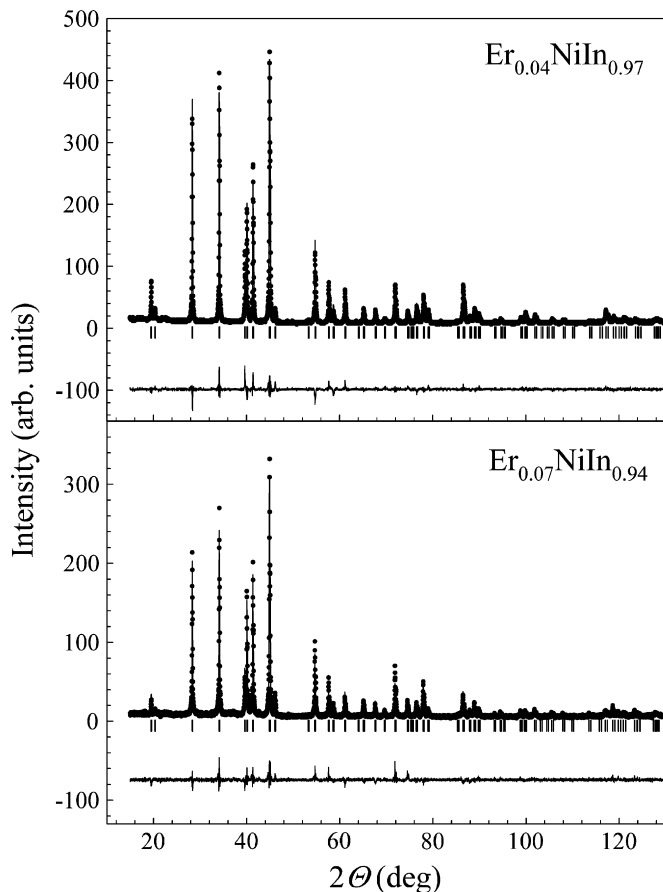


Fig. 7. Observed (\blacklozenge) calculated (—) and difference X-ray diffraction patterns of the $Er_{0.04}NiIn_{0.97}$ and $Er_{0.07}NiIn_{0.94}$ (Seifert XRD7 diffractometer, Cu- $K\alpha$ radiation).

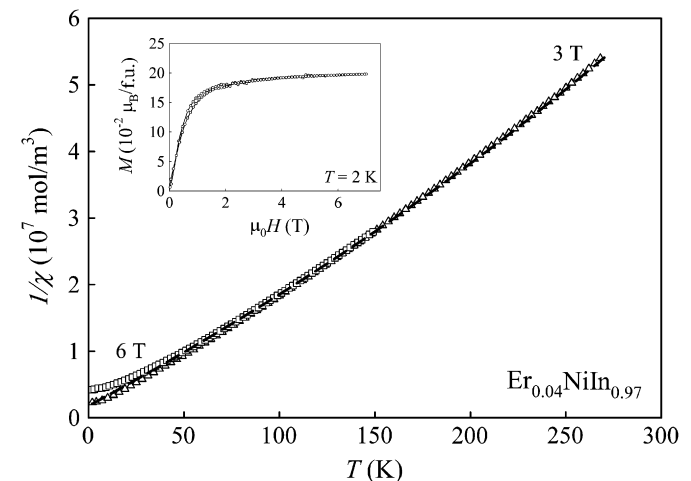


Fig. 9. Temperature dependence of inverse susceptibility in $Er_{0.04}NiIn_{0.97}$, measured in $\mu_0H=3$ T (triangles) and 6 T (squares). The dashed line represents the modified CW fit. Inset: DC magnetization versus magnetic field.

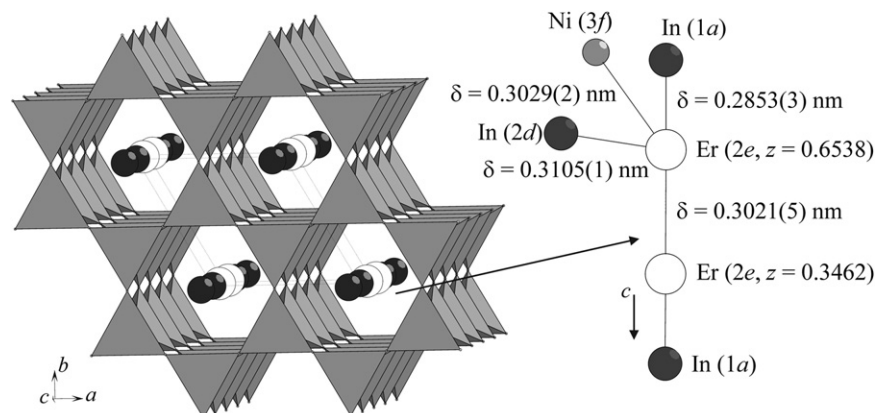


Fig. 8. Close packing of the empty tetrahedra $[In(2d)3Ni(3f)]$ and sequence of voids occupied by In- and Er-atoms and arrangement of Er atoms along the c -direction in $Er_{0.07}NiIn_{0.94}$.

the Er–Ni–In system. The extended homogeneity region of the $\text{ErNi}_{1-0.60}\text{In}_{1-1.40}$ ternary compounds (ZrNiAl-type structure) with substitution of Ni by In exists in Er–Ni–In system. The $\text{RNi}_{1-x}\text{In}_{1+x}$ compounds with $R=\text{Gd, Tb, Dy, Ho, and Tm}$ also form the homogeneity regions [14,15,22]. In the same time, the compound with this type structure exists in Ce–Ni–In system, but has equiatomic composition. The distinctive feature of Er–Ni–In system is presence of mutual solubilities of ErNi_2 (MgCu₂-type structure) and ErNi_4In (MgCu₄Sn-type structure) phases along 66.7% cross section of Ni. The ternary ErNi_4In can be derived from ErNi_2 by substitution of half of Er atoms on In atoms in elementary cell by the scheme: $8\text{ErNi}_2=\text{Er}_8\text{Ni}_{16}=\text{Er}_4\text{Er}_4\text{Ni}_{16}=\text{Er}_4\text{In}_4\text{Ni}_{16}=4\text{ErNi}_4\text{In}$. The substitution of Er-atoms for In-atoms is possible due to the small difference of atomic radii of these atoms (0.1757 and 0.1663 nm for Er and In, respectively) [23]. A similar situation is observed in the Tm–Ni–In system, in which TmNi_4In forms a continuous series of solid solutions with TmNi_2 [24]. Also formation of small homogeneity region of YbCu_4In across the Cu cross section was reported earlier on [25]. As rule, the compounds RCu_4In ($R=\text{Y, Nd, Sm, and Gd-Lu}$) form a continuous series of solid solutions with the RCu_5 compounds (AuBe₅ structure type), and in the homogeneity region of these compounds the Cu-atoms are replaced by In atoms [26]. The possibility of substitution of Er-atoms for In-atoms confirms the existence of statistic mixture (Er+In) in the $\text{Er}_{2.30}\text{Ni}_{1.84}\text{In}_{0.70}$ and $\text{Er}_{13.53}\text{Ni}_{3.14}\text{In}_{3.33}$ compounds.

One more interesting fact is the existence of including-substitution type solid solution based on NiIn binary compound. Practically the same situation is observed in R–Pd–In systems ($R=\text{Gd-Er}$), where the large range of solid solutions $\text{R}_x\text{PdIn}_{1-x}$ (for Er $x=0-0.57$) starting from the binary PdIn (CsCl-type structure) was described [27].

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