ELSEVIER

Journal of Alloys and Compounds 234 (1996) 151–156

Journal of ALLOYS AND COMPOUNDS

Ce–Fe–Ge, Nd–Fe–Ge and Ho–Fe–Ge phase diagrams: systematics of rare earth–iron–germanium compounds ☆

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Received 20 June 1995

Abstract

The ternary systems Ce(Nd,Ho)–Fe–Ge have been investigated and phase relations have been determined at 870 K, where respectively seven, eight and six compounds were observed. A critical assessment on the interaction of rare earth elements with iron and germanium has been made.

Keywords: Phase diagrams; Ternary rare earth compounds; R–Fe–Ge compounds; Crystal structure

1. Introduction

The observation of $Nd_2Fe_{14}B$ [1] with unique magnetic properties has stimulated an intensive investigation of ternary alloys containing rare earth, transition metals and elements of III, IV and V groups.

At present the ternary systems R–Fe–Ge, R = Pr, Tm [2], Sm [3], Eu [4], Tb [5], Er [6], Yb [7] have been completely investigated by co-workers of the Inorganic Chemistry Department of the L'viv University. The ternary systems Ce–Fe–Ge, Nd–Fe–Ge and Ho–Fe–Ge have partially been investigated with respect to the formation and crystal structure of ternary compounds. Also, phase diagram details have been studied. The compounds reported in the literature correspond to the following compositions: Ce(Nd)Fe_2Ge_2 ($CeGa_2Al_2$ type) [8], Ce(Nd,Ho)$Fe_{1-x}Ge_2$ ($CeNiSi_2$ type) [9], Nd(Ho)Fe_6Ge_6 (YCo_6Ge_6 type) [10], $Nd_6Fe_{13}Ge$ ($Nd_6Fe_{13}Si$ type) [11], $NdFe_{0.67}Ge_{1.33}$ (AlB_2 type) [12], $HoFe_4Ge_2$ ($ZrFe_4Si_2$ type) [2] and $Ho_6Fe_8Ge_8$ ($Gd_6Cu_8Ge_8$ type) [13]. The results of X-ray investigations of the phase relations in Ce–Fe–Ge, Nd–Fe–Ge and Ho–Fe–Ge systems at 870 K are summarized in this paper.

The binaries involved in the Ce–Fe–Ge, Nd–Fe–Ge and Ho–Fe–Ge systems were studied sufficiently and form a large number of intermetallic compounds. Crystallographic data of binary phases are listed in Table 1.

2. Experimental details

The ternary samples used to derive the phase relations in the ternary sections at 870 K, each with a total weight of 2 g, were synthesized by arc melting proper amounts of the constituent elements under high purity argon on a water-cooled copper hearth. The starting materials were used in the form of ingots of high purity elements — cerium, neodymium, holmium (99.9%), iron (99.99%), germanium (99.999%). The weight losses were generally less than 1%. The alloys were annealed at 870 K in evacuated quartz tubes for 2 weeks and quenched in water.

The identification of the various phases present in each sample was made by examination of the X-ray powder patterns (Debye–Scherrer photographs, RKD-57.3 cameras, nonfiltered Cr K-radiation). In view of the number of phases occurring in the concentration range containing 20–30 at.% Ce, 5–20 at.% Fe, 55–65 at.% Ge, a combined X-ray and micrography examination was essential. The microstructure of the alloys was revealed by etching in a dilute solution of HCl and HF. Metallographic examinations were carried out using standard technique (microscope MIM-8). The

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SSDI 0925-8388(95)02034-9

Table 1
Crystallographic data of compounds of binary (Ce, Nd, Ho)–Fe, Fe–Ge and (Ce, Nd, Ho)–Ge systems

Compound	Structure type	Space group	Lattice parameters (nm)			Reference
			a	*b*	*c*	
$CeFe_2$	$MgCu_2$	*Fd3m*	0.7303			[14]
α-Ce_2Fe_{17}	Th_2Ni_{17}	*P6₃/mmc*	0.8940		0.8281	[14]
β-Ce_2Fe_{17}	Th_2Zn_{17}	*R3m*	0.8490		1.2416	[14]
Nd_2Fe_{17}	Th_2Zn_{17}	*R3m*	0.858		1.2458	[15]
Nd_5Fe_{17}	Nd_5Fe_{17}	*P6₃/mmc*	2.0219		1.233	[16]
$HoFe_2$	$MgCu_2$	*Fd3m*	0.7305			[17]
$HoFe_3$	$PuNi_3$	*R3m*	0.5084		2.445	[17]
Ho_6Fe_{23}	Th_6Mn_{23}	*Fm3m*	1.2032			[17]
Ho_2Fe_{17}	Th_2Ni_{17}	*P6₃/mmc*	0.8438		0.8310	[17]
Fe_3Ge(HT)	Ni_3Sn	*P6/mmc*	0.5162		0.4207	[18]
Fe_3Ge(LT)	Cu_3Sn	*Pm3m*	0.3574			[18]
$Fe_{3.2}Ge_2$	$Fe_{3.2}Ge_2$	*P6₃/mmc*	0.3998		0.5010	[18]
$Fe_{13}Ge_8$	$Fe_{13}Ge_8$	*P6₃/mmc*	0.7976		0.4993	[18]
Fe_6Ge_5	Fe_6Ge_5	*C2/m*	0.9965	0.7826 $\beta = 109.66°$	0.7801	[18]
FeGe	CoSn	*P6/mmm*	0.4965		0.4045	[18]
$FeGe_2$	$CuAl_2$	*I4/mcm*	0.5908		0.4957	[18]
Ce_3Ge	Ti_3P	*P4₂/n*	1.2482		0.6137	[19]
Ce_5Ge_3	Mn_5Si_3	*P6₃/mmc*	0.888		0.661	[19]
Ce_4Ge_3	Th_3P_4	*I43d*	0.9214			[19]
Ce_5Ge_4	Sm_5Ge_4	*Pnma*	0.795	1.522	0.806	[19]
CeGe	FeB	*Pmna*	0.832	0.407	0.602	[19]
β-$CeGe_{2-x}$	α-$ThSi_2$	*I4₁/amd*	0.4259		1.4280	[19]
α-$CeGe_{2-x}$	α-$GdSi_2$	*Imma*	0.4278	0.4215	1.4071	[19]
Nd_5Ge_3	Mn_5Si_3	*P6₃/mcm*	0.875		0.655	[20]
Nd_5Ge_4	Sm_5Ge_4	*Pnma*	0.785	1.510	0.794	[20]
NdGe	CrB	*Cmcm*	0.422	1.097	0.404	[20]
β-$NdGe_{2-x}$	α-$ThSi_2$	*I4₁/amd*	0.423		1.415	[20]
α-$NdGe_{2-x}$	α-$GdSi_2$	*Imma*	0.422	0.417	1.403	[20]
Ho_5Ge_3	Mn_5Si_3	*P6₃/mcm*	0.8391		0.6295	[21]
Ho_5Ge_4	Sm_5Ge_4	*Pnma*	0.7568	1.4569	0.7648	[21]
$Ho_{11}Ge_{10}$	$Ho_{11}Ge_{10}$	*I4/mmm*	1.0818		1.6247	[21]
HoGe	CrB	*Cmcm*	0.42428	1.0623	0.3919	[21]
$HoGe_4$	W_3CoB_3	*Cmcm*	0.4012	1.0562	1.4120	[22]
α-$HoGe_{1.5}$	AlB_2	*P6/mmm*	0.3926		0.4113	[21]
α-$HoGe_{1.7}$	unknown					[21]
β-$HoGe_{1.7}$	α-$ThSi_2$	*I4₁/amd*	0.4044		1.362	[21]
$HoGe_{1.8}$	$DyGe_{1.85}$	*Cmc2₁*	0.4082	2.9559	0.3918	[23]
$HoGe_{2.7}$	unknown					[21]

microhardness (PMT-3) was measured for five predominantly single phase Ce–Fe–Ge samples.

The crystal structure was determined by a least squares refinement using powder diffraction data (DRON-3.0 diffractometer, Cu Kα radiation). All the procedures, including indexing, lattice and atomic parameter refinement, were accomplished using the CSD program package [24].

3. Results

3.1. The Ce–Fe–Ge system

The information obtained using the techniques outlined in the preceding section enable us to construct the isothermal section of the Ce–Fe–Ge system at 870 K (Fig. 1(a)). The main result is the identification of seven ternary compounds, the crystal structure has been determined for three of them. Crystallographic information on the ternary compounds is summarized in Table 2. Mutual solid solubilities of the binary compounds are insignificantly small.

3.2. The Nd–Fe–Ge system

Fig. 1(b) reports the isothermal section of Nd–Fe–Ge system at 870 K as derived from X-ray phase analysis. The phase field distribution is characterized by the presence of eight ternary compounds. Crystallographic data of the ternary phases of Nd–Fe–Ge system are listed in Table 3.

Mayer and Felner [12] and Weitzer et al. [11] reported the crystal data for $NdFe_{0.67}Ge_{1.33}$ and

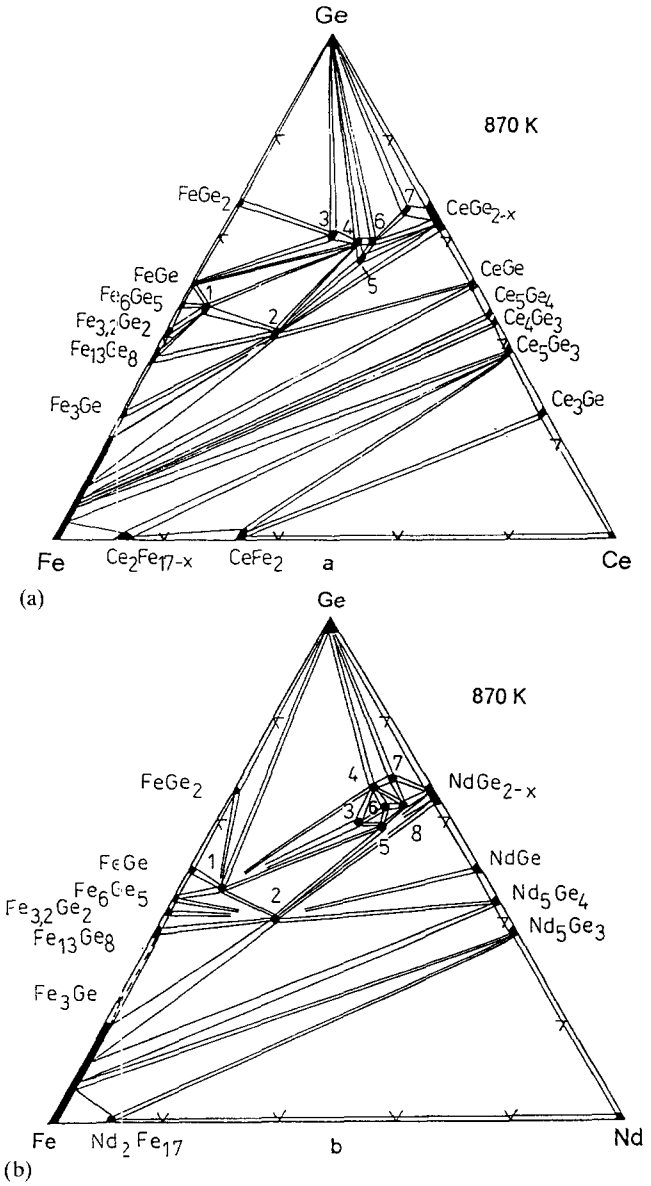

Fig. 1. Isothermal sections of the Ce–Fe–Ge (a) and Nd–Fe–Ge (b) systems at 870 K.

$Nd_6Fe_{13}Ge$. These compounds have not been observed at 870 K; therefore, it is possible that they exist only within a limited temperature range.

The binary compound Fe_3Ge does not appear in Nd–Fe–Ge ternary. None of binary phases show appreciable ranges of mutual solid solubility.

3.3. The Ho–Fe–Ge system

Six intermetallic compounds have been observed in this system at 870 K (see Table 4). The constitutional diagram is shown in Fig. 2.

The binary compounds $HoGe_{2.7}$ and $HoGe_{1.7}$ do not appear in Ho–Fe–Ge ternary at 870 K.

4. Discussion

The primary intention of this section is the comparison of interaction of components in R–Fe–Ge systems, where R is a rare earth metal. According to Sections 1 and 3, we take account of, in general, ten ternary systems, for which the phase equilibria have been investigated.

From the results obtained in this research and the literature data [2–7,25] some common regularities of the interaction of rare earth metals with iron and germanium can be drawn. The number of ternary compounds formed with light rare earth elements, iron and germanium monotonously increases from lanthanum to samarium. No ternary compounds were found with europium. Among the heavy lanthanides, thulium forms the largest number of ternary compounds with iron and germanium (see Fig. 3).

The ternary systems R–Fe–Ge are characterized by various stoichiometries and crystal structures of the existing ternary compounds, depending on the rare earth metal (Table 5). As one can see, the most prevailing structure types are $CeGa_2Al_2$ and $CeNiSi_2$. The compounds with AlB_2-, $BaNiSn_3$-, $Nd_6Fe_{13}Si$- and $Sm_4Co_{1-x}Ge_7$-type were observed in ternary systems containing light lanthanides, the compounds with $CeGa_2Al_2$-, $CeNiSi_2$-, YCo_6Ge_6- and $Tb_{117}Fe_{52}Ge_{112}$-

Table 2
Crystallographic data and microhardness of ternary Ce–Fe–Ge compounds at 870 K

N	Compound	Structure type	Space group	Lattice parameters (nm)			Microhardness (kg mm^{-2})	Reference
				a	*b*	*c*		
1	~$CeFe_{10}Ge_6$	unknown						—[a]
2	$CeFe_2Ge_2$	$CeGa_2Al_2$	*I4/mmm*	0.4070(2)		1.0883(3)		[8][a]
3	$CeFeGe_3$	$BaNiSn_3$	*I4mm*	0.4339(1)		0.9974(3)	488	—[a]
4	~$Ce_3Fe_2Ge_7$	unknown					273	—[a]
5	$CeFe_{0.64}Ge_2$	$CeNiSi_2$	*Cmcm*	0.4278(1)	1.6608(8)	0.4150(2)	386	[9][a]
6	~Ce_2FeGe_4	unknown					271	—[a]
7	~Ce_6FeGe_{13}	unknown					351	—[a]

[a] The results of this work.

Table 3
Crystallographic data of ternary Nd–Fe–Ge compounds at 870 K

N	Compound	Structure type	Space group	Lattice parameters (nm)			Reference
				a	*b*	*c*	
1	$NdFe_6Ge_6$	YCo_6Ge_6	*P6/mmm*	0.5142(1)		0.4049(2)	[10][a]
2	$NdFe_2Ge_2$	$CeGa_2Al_2$	*I4/mmm*	0.4038(1)		1.0510(2)	[8][a]
3	~$Nd_5Fe_3Ge_{12}$	unknown					—[a]
4	~$Nd_5Fe_2Ge_{13}$	unknown					—[a]
5	$NdFe_{0.37}Ge_2$	$CeNiSi_2$	*Cmcm*	0.4214(1)	1.6450(8)	0.4084(1)	[9][a]
6	~Nd_3FeGe_7	unknown					—[a]
7	~Nd_4FeGe_{10}	orthorhombic		0.422(2)	0.403(7)	2.828(4)	—[a]
8	$Nd_4Fe_{0.64}Ge_7$	$Sm_4Co_{1-x}Ge_7$	*Amm2*	0.4198(2)	0.4095(3)	3.037(8)	—[a]

[a] The results of this work.

Table 4
Crystallographic data of ternary Ho–Fe–Ge compounds at 870 K

N	Compound	Structure type	Space group	Lattice parameters (nm)			Reference
				a	*b*	*c*	
1	$HoFe_6Ge_6$	YCo_6Ge_6	*P6/mmm*	0.5110(2)		0.4056(1)	[10][a]
2	$HoFe_4Ge_2$	$ZrFe_4Si_2$	$P4_2/mnm$	0.7255(3)		0.3852(3)	[2][a]
3	$HoFe_2Ge_2$	$CeGa_2Al_2$	*I4/mmm*	0.3949(1)		1.0430(3)	[8][a]
4	$Ho_6Fe_8Ge_8$	$Gd_6Cu_8Ge_8$	*Immm*	1.3450(7)	0.6781(4)	0.4117(2)	[13][a]
5	$HoFe_{0.33}Ge_2$	$CeNiSi_2$	*Cmcm*	0.4102(1)	1.5689(4)	0.3986(1)	[9][a]
6	$Ho_{117}Fe_{52}Ge_{112}$	$Tb_{117}Fe_{52}Ge_{112}$	*Fm3m*	2.8238(9)			—[a]

[a] The results of this work.

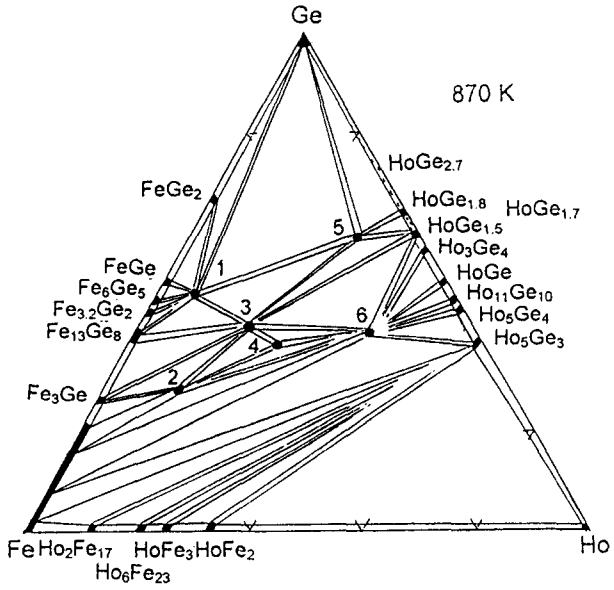

Fig. 2. Isothermal section of the Ho–Fe–Ge system at 870 K.

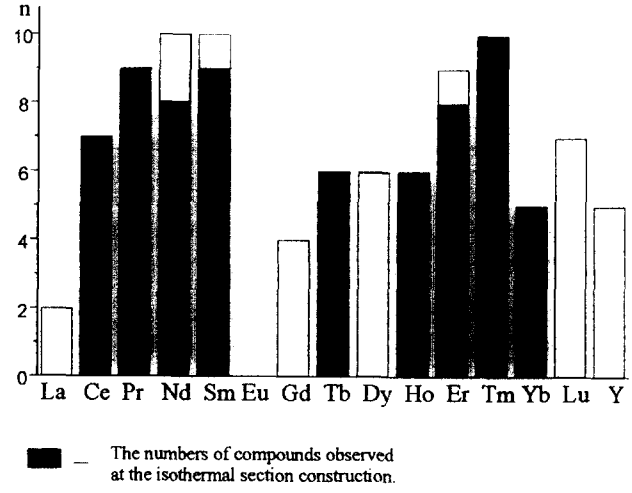

Fig. 3. The numbers *n* of the existing compounds in ternary systems R–Fe–Ge.

type are found for light and heavy rare earth elements; $ZrFe_4Si_2$-, $Gd_6Cu_8Ge_8$-, $Tm_9Fe_{10}Ge_{10}$- and $Hf_3Ni_2Si_3$-types are typical only for heavy lanthanides.

The range of formation of ternary R–Fe–Ge compounds is restricted to concentrations of less than 42 at.% rare earth metal; $R_{117}Fe_{52}Ge_{112}$ ($Tb_{117}Fe_{52}Ge_{112}$-type) is the terminal R-rich phase. Fig. 4 schematically shows the distribution of compounds over the R–Fe–Ge ternary sections at 870 K. Ternary compounds with light lanthanides are found predominantly in the range 40–70 at.% Ge, whereas the heavy rare earth elements

Table 5
Ternary R–Fe–Ge compounds with solved crystal structure[a]

Structure type	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	Reference
$CeGa_2Al_2$	+	+	+	+	+	–	+	+	+	+	+	+	+	+	+	[25][b]
$CeNiSi_2$	–	+	+	+	+	–	+	+	+	+	+	+	+	+	+	[9][b]
YCo_6Ge_6	–	–	+	+	+	–	+	+	+	+	+	+	+	+	+	[10][b]
$Tb_{117}Fe_{52}Ge_{112}$		–	+	–	+	–		+	+	+	+	+	–	+	+	[2,3,6][b]
$ZrFe_4Si_2$		–	–	–	–	–	–	+	+	+	+	+	+	+	+	[2,6,7][b]
$Gd_6Cu_xGe_y$		–	–	–	–	–	–	–	+	+	+	+	–	+	–	[13][b]
$Hf_3Ni_2Si_3$		–	–	–	–	–		–		–	+	–	–	+		[2,6]
$Tm_6Fe_{10}Ge_{10}$		–	–	–	–	–		–		–	+	+	+			[2,6,7]
$BaNiSn_3$		+	+	–	–	–		–		–	–	–	–			[2][b]
AlB_2	+	–	–	+	+	–		–		–	–	–	–			[25]
$Nd_6Fe_{13}Si$		–	+	+	–	–		–		–	–	–	–			[11]
$Sm_4Co_{1-x}Ge_7$		–	+	+	+	–		–		–	–	–	–			[2,3][b]

[a] + indicates the compound exists; – indicates the compound was not observed; no table entry means that the alloy of corresponding composition was not investigated.
[b] The results of this work.

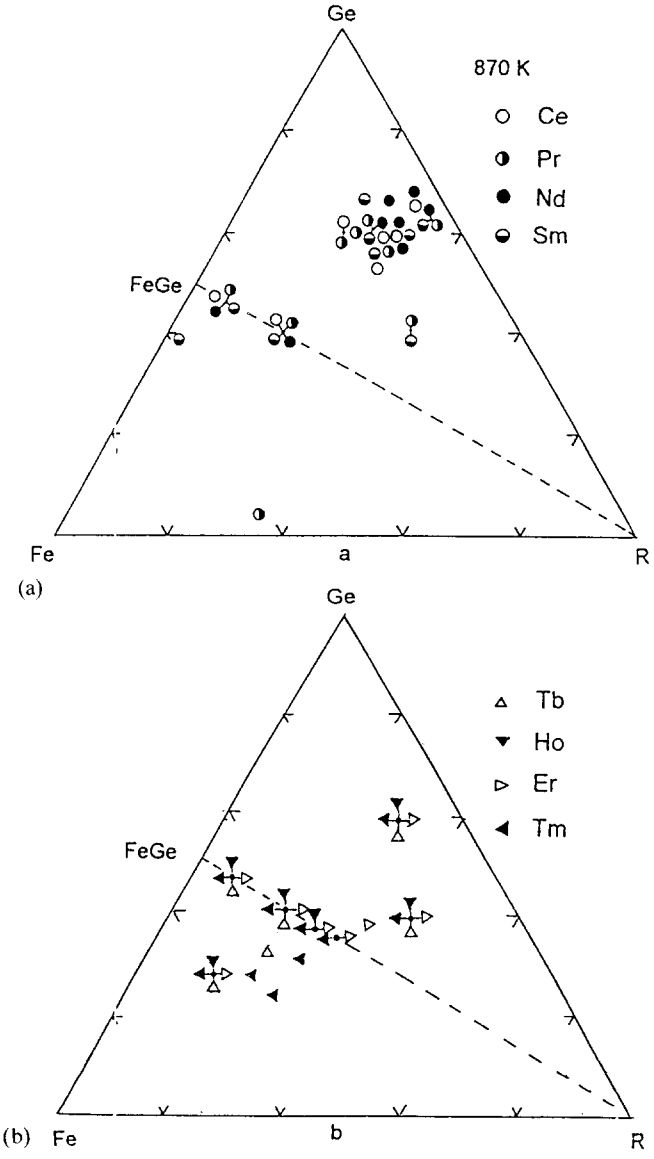

Fig. 4. Schematic diagram showing the position of ternary compounds in the systems for which phase equilibria have been investigated: (a) R–Fe–Ge, R = Ce, Pr, Nd, Sm; (b) R–Fe–Ge, R = Tb, Ho, Er, Tm.

form compounds primarily in the concentration region from 28 to 50 at.% Ge.

References

[1] D. Givord, H.S. Li and J.M. Moreau, *Solid State Commun., 50* 6 (1984) 497.
[2] M.F. Fedyna, *Ph.D. Chemistry Thesis*, L'viv, 1988.
[3] O.Ya. Mruz, *Ph.D. Chemistry Thesis*, L'viv, 1988.
[4] B.D. Belan, *Ph.D. Chemistry Thesis*, L'viv, 1988.
[5] P.K. Starodub, *Ph.D. Chemistry Thesis*, L'viv, 1988.
[6] O.Ya. Oleksyn, *Ph.D. Chemistry Thesis*, L'viv, 1990.
[7] R.O. Dzyanyj, O.I. Bodak and V.V. Pavlyuk, *Izv. RAN Metall.*, in press.
[8] D. Rossi, R. Marazza and R. Ferro, *J. Less-Common Met., 58* (2) (1978) 203.
[9] V.K. Pecharsky, O.Ya. Mruz, M.B. Konyk, P.S. Salamakha, P.K. Starodub, M.F. Fedyna and O.I. Bodak, *J. Structur. Khim., 30* (5) (1989) 96.
[10] O.Ya. Mruz and P.K. Starodub, *Dopov. AN URSR B, 12* (1984) 44.
[11] F. Weitzer, R. Klesnar and P. Rogl, *Int. Conf. Light Metals, Collected Abstracts, Amsterdam, 1990*, p. 577.
[12] I. Mayer and J. Felner, *J. Less-Common Met., 29* (1) (1972) 25.
[13] M.F. Fedyna, O.Ya. Oleksyn, N.S. Bilonishko and O.V. Gulyak, *Visnyk L'viv University, 33* (1994) 53.
[14] K.H.J. Buschow and J.S. Wieringen, *Phys. Status Solidi, 42* (1) (1970) 231.
[15] G. Schneider, E. Henig, G. Petzow and H. Stadelmeier, *Z. Metallkd., 78* (10) (1987) 694.
[16] J.M. Moreau, L. Paccard, J.P. Nozveres, F.P. Missell, G. Schneider and V. Villas-Boos, *J. Less-Common Met., 163* (2) (1990) 245.
[17] E.I. Gladyshevsky and O.I. Bodak, Krystollokhimiya *Intermetallicheskikh Soedin. Redkozemelnykh Metallov*, Vyshcha shkola, L'viv, 1982.
[18] O. Kubaschewski, *Iron—Binary Phase Diagrams*, Springer, Berlin, 1982.
[19] V.N. Eremenko, Z.K. Schi, Yu.I. Buyanow and A.M. Khar-'kova, *Dopov. AN URSR B, 12* (1972) 1080.
[20] V.N. Eremenko, V.G. Batalin and Yu.I. Buyanov, *Izv. AN SSSR, Neorgan. Mater., 10* (8) (1984) 1384.

[21] V.N. Eremenko and I.M. Obushenko, *Izv. Vuzov. Zvet. Met., 3* (1981) 59.
[22] O.Ya. Oleksyn and O.I. Bodak, *J. Alloys Comp., 210* (1994) 19.
[23] Z.M. Shpyrka, *Ph.D. Chemistry Thesis*, L'viv, 1991.
[24] L.G. Aksel'rud, Yu.N. Grin, P.Yu. Zavalij, V.K. Pecharsky and V.S. Fundamensky, *XII European Crystallography Meet. Collected Abstracts, Moscow, 1989*, p. 155.
[25] E.I. Gladyshevsky, O.I. Bodak and V.K. Pecharsky, *Handbook on the Physics and Chemistry of Rare Earth*, Amsterdam, 1990, p. 13.