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Isothermal Cross-Sections of Gd-Fe-Ge System at 800 °C and Magnetic Properties of $Gd_{117}Fe_{52}Ge_{112}$ Compound

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The isothermal section of the phase diagram of the Gd-Fe-Ge ternary system at 800 °C was investigated by X-ray powder diffraction and scanning electron microscope-energy dispersive X-ray spectroscopy. Three intermediate solid solutions have been identified or confirmed: one lacunaire $GdFe_xGe_2$ ($CeNiSi_2$-type of structure space group P6/mmm) and two by substitition $GdFe_{4-x}Ge_x$ (AlB_4-type of structure space group I4/mmm) and $GdFe_{12-x}Ge_x$ (YCo_6Ge_6-type of structure space group P6/mmm) and one ternary compound $Gd_{117}Fe_{52}Ge_{112}$ ($Tb_{117}Fe_{52}Ge_{112}$-type of structure space group Fm-3m). The magnetic properties of $Gd_{117}Fe_{52}Ge_{112}$ compound is ferromanetic at 89 K have been studied. The 800 °C phase diagram of this system consists of 20 three-phases regions.

Keywords: Magnetic, Intermetallic compounds, Phase diagram, X-ray diffraction.

INTRODUCTION

The investigation on the intermetallic compounds in RE-Fe-M (RE = rare earth metal, M = Si, Al, Cr, V, Ti, Nb, Mo and W) is of scientific and technical interest. Because of their magnetic properties, many scientists have reported these compounds in order to find new permanent magnetic materials [1,2]. Magnetic refrigeration is becoming a promising technology to replace the conventional gas-compression refrigeration due to its high efficiency, energy saving and environmental concerns [3,4]. Particularly, the magnetic refrigeration used near room temperature in a low magnetic field has attracted much attention for its potentiel application in many areas [5,6]. The prototype magnetic refrigeration material for near room temperature is Gd with the curie tempe-rature Tc at 293K. The trends of these properties have been points of interest to investigate RE-Fe-X systems especially Gd based systems in searching of highly efficient magnetic working materials, which is critical for the magnetic cooling technology.

The ternary systems R-Fe-Ge, (R = Pr, Tm, Sm, Eu, Tb, Er, Yb, Nd, Ho, Ce [7], La [8] have been completely investigated. The phase diagram of the Gd-Fe-Ge ternary system at 500 °C has been reported by Zhuang *et al.* [9] who mentioned that a part of this diagram was already done at 800 °C by our group [10]. As part of our systematic search of new interesting intermalallic compounds in this area, we present the results obtained in the investigation of the isothermal section at 800 °C of Gd-Fe-Ge phases diagram. The following intermetallic compounds are already known from the literature: $GdFe_{0.37}G_2$($CeNiSi_2$-type of structure space group P6/mmm) [11], $GdFe_2Ge_2$ (AlB_4-type of structure space group I4/mmm) [12], $GdFe_6Ge_6$ (YCo_6Ge_6-type of structure space group P6/mmm) [13] and $Gd_{117}Fe_{52}Ge_{112}$ ($Tb_{117}Fe_{52}Ge_{112}$-type of structure space group Fm-3m) [14].

EXPERIMENTAL

The investigation of the phase equilibria in the Gd-Fe-Ge system, has been realized over more than 90 samples each with a total weight of 0.5 g were prepared by arc melting the constitution elements under high purity argon atmosphere using a non-consumable tungsten electrode on a water-cooled copper hearth crucible and a zirconium piece as oxygen getter. The starting materials were the high purity metals gadolinium (Gd: 99.99 mass % purity), germanium (Ge:99.9 mass % purity) and iron (Fe: 99.9 mass % purity). The weight losses during melting were lower than 1 %.

All alloys after melting enclosed under vacuum in flame sealed silica ampoules, were annealed at 800 °C for 1 week in a resistance furnace and then quenched to room temperature.

X-ray diffraction powder patterns were collected at room temperature using a Inel CPS 120 diffractometer, with CoK$_\alpha$ radiation ($\lambda = 1.789007$ Å). The microstructure of the samples was studied on polished surfaces using a Jeol JSM 6400 scanning electron microscope (SEM). The composition of the phases was analyzed by energy dispersive spectroscopy (EDS) with an Oxford Link-Isis Si/Li analyzer. They phases diagram were mainly determined by X-ray diffraction analysis. The phases in some alloys were determined by electron-probe microanalysis in order to determine the maximal solubility of the single phase. By comparing and analyzing the X-ray patterns and metallographic examination of the samples annealed for the above periods of time, it was shown that the phases in the alloys completely reached equilibrium.

RESULTS AND DISCUSSION

Binary systems: The information obtained using the techniques outlined in the preceding section largely confirms the findings of previous binary phases of the Gd-Fe-Ge system at 800 °C. The partial isothermal section contains eleven binary phases and a solubility range of the unary α-Fe into the binary FeGe field up to about 20 at % Ge, stable at 800 °C. the crystal structure data relevant to the unary [15-17] and binary boundry phases [18-20] in this system are listed in Table-1. In the Fe-Ge system, regarding the limits of the homogeneity ranges of the solid solutions, our analyses roughly confirm the reported values of the binary $Fe_{100-x}Ge_x$ solid solutions with $x \leq 20$, $24 \leq x \leq 26.4$ and $35 \leq x \leq 40.2$. In the Gd-Ge system side, we confirme the existance of the known four binary phases Gd_5Ge_3, Gd_5Ge_4, GdGe and Gd_2Ge_3 which are stable phases at 800 °C. A binary solid solution of $Gd_{100-x}Ge_x$ is defined in the homogeneity range $60 \leq x \leq 63$. The Fe-Gd binary boundary of the Gd-Fe-Ge system at 800 °C depicts the following compounds, βGd_2Fe_{17} (hexagonal Th_2Fe_{17}-type of structure), Gd_2Fe_{23} (cubic Th_6Mn_{23} type structure), $GdFe_3$ (rhombohedral Ni_3Pu type structure) and $GdFe_2$ (cubic $MgCu_2$ type structure).

Isothermal section: Based on the results of the metallurgical analysis of selected samples and the phase analysis of XRD patterns of all samples, the 800 °C isothermal section of the Gd-Fe-Ge ternary system was determined (Fig. 1).

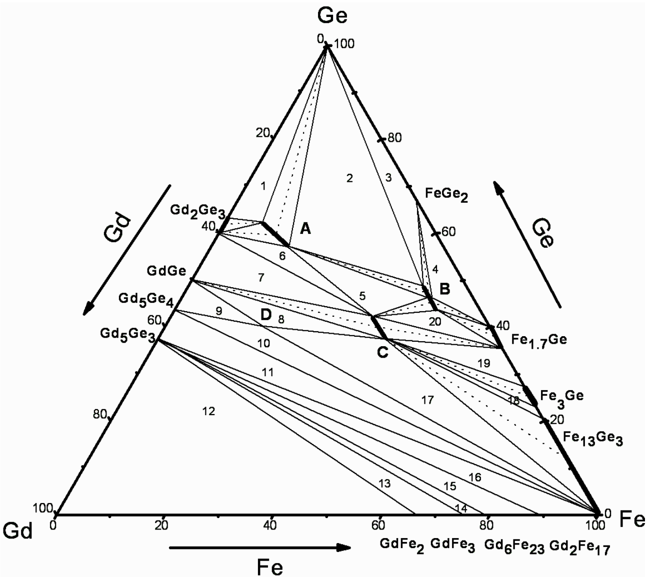

Fig. 1. Isothermal section of Gd-Fe-Ge ternary system at 800 °C

This isotermal section consists of 19 single-phase regions, 37 two-phases regions and 20 three-phases regions. Details of the three-phase region are given in Table-2.

The Gd-Fe-Ge system is charaterized by the absence of extend solid solution based on binary in the ternary. One ternary intermetallic defined compound of formula $Gd_{117}Fe_{52}Ge_{112}$ and three ternary solid solutions have been observed in this isothermal section.

$ErFe_{12-x}Ge_x$ and $ErFe_{4-x}Ge_x$ phases form more or less extended solid solution at constant rare earth composition due to the substitution between Ge and Fe atoms in the crystal

TABLE-1
CRYSTALLOGRAPHIC DATA OF COMPOUNDS OF BINARY Gd-Fe, Fe-Ge AND Gd-Ge

Compound	Structure type	Space group	Lattice parameters (Å)			Ref.
			a	b	c	
GdGe	BCr	Cmcm	4.3390	10.788	3.973	[18]
$Gd_2G\ e_3$	Si_2Th	$I4_1amd$	4.1000		13.730	[18]
$Gd_5G\ e_4$	Sm_5Ge_4	Pnma	7.6900	14.750	7.760	[18]
$Gd_5G\ e_3$	Mn_5Si_3	$P6_3/mmc$	8.5500		6.400	[18]
FeGe2	$CuAl_2$	I4/mcm	5.9080		4.957	[17]
Fe_3Ge (HT)	Ni_3Sn	P6/mmm	5.1620		4.207	[17]
Fe_3Ge (LT)	Cu_3Sn	Pm3m	3.5740			[17]
$Fe_{1.7}Ge$	Ni_2In	$P6_3/mmc$	4.0310		5.022	[17]
$Fe_{13}Ge_3$	$Fe_{13}Ge_3$	Pm3m	5.7630			[17]
$GdFe_2$	$MgCu_2$	Fd-3m	7.3800			[19]
GdFe3	Be_3Nb	R-3m	5.1480			[19]
Gd_6Fe_{23}	Th_6Mn_{23}	Fm-3m	12.1200			[19]
Gd_2Fe_{17}	$TbCu_7$	P6/mmm	4.9070		4.110	[19]
Gd_2Fe_{17}	Th_2Ni_{17}	$P6_3/mmc$	8.5170		8.345	[19]
Gd_2Fe_{17}	Th_2Zn_{17}	R-3m	8.4960			[19]
Fe (α)	W	Im-3m	2.8665			[14]
Fe (γ)	Cu	Fm-3m	3.6599			[14]
Fe (δ)	W	Im-3m	2.9315			[14]
Gd	Mg	$P6_3/mmc$	3.6300		5.780	[15]
Ge	C	Fd3m	5.6500			[16]

TABLE-2
DETAILS OF THE THREE-PHASE REGIONS IN THE ISOTHERMAL SECTION OF PHASE DIAGRAM Gd-Fe-Ge TERNARY SYSTEM AT 1073 K

Phase region	Alloy composition (at %)			Phase compositions
	Gd	Fe	Ge	
1	25	3	70	$Gd_2Fe_3 + Gd_3Fe_1Ge_6 + Ge$
2	15	20	30	$Gd_3Fe_1Ge_6 + GdFe_6Ge_6 + Ge$
3	2	25	75	$GdFe_6Ge_6 + FeGe_2 + Ge$
4	2	25	25	$GdFe_6Ge_6 + FeGe_2 + Fe_{1.7}Ge$
5	20	45	55	$Gd_3Fe_1Ge_6 + GdFe_6Ge_6 + GdFe_2Ge_2$
6	30	20	55	$Gd_3Fe_1Ge_6 + GdFe_2Ge_2 + Gd_2Ge_3$
7	20	10	30	$GdFe_2Ge_2 + Gd_2Fe_3 + GdGe$
8	27	15	30	$GdFe_2Ge_2 + GdGe + Gd_{117}Fe_{52}Ge_{112}$
9	50	5	45	$Gd_{117}Fe_{52}Ge_{112} + Gd_5Ge_4 + GdGe$
10	46	20	40	$Gd_{117}Fe_{52}Ge_{112} + Gd_5Ge_4 + Fe(\alpha)$
11	43	20	30	$Gd_5Ge_4 + Gd_5Ge_3 + Fe(\alpha)$
12	80	20	30	$Gd_5Ge_3 + GdFe_2 + Gd$
13	40	50	12	$GdFe_2 + GdFe_3 + Gd_5Ge_3$
14	40	50	15	$Gd_5Ge_3 + GdFe_3 + Gd_6Fe_{23}$
15	40	60	17	$Gd_5Ge_3 + Gd_2Fe_{17} + Gd_6Fe_{23}$
16	40	90	20	$Gd_5Ge_3 + Gd_6Fe_{23} + Gd_2Fe_{17}$
17	25	40	35	$Gd_{117}Fe_{52}Ge_{112} + GdFe_2Ge_2 + Fe(\alpha)$
18	5	70	25	$GdFe_2Ge_2 + Fe_3Ge + Fe(\alpha)$
19	7	60	32	$GdFe_2Ge_2 + Fe_3Ge + Fe_{1.7}Ge$
20	10	63	50	$GdFe_2Ge_2 + GdFe_6Ge_6 + Fe_{1.7}Ge$

lattice; their homogeneity fields are practically linear, parallel to the Ge-Fe axis; the third solid solution $GdFe_xGe_2$ has defect structure model with the Fe positions which are not full occupied. Crystal structure and lattice parameters data of ternary phases of the Gd-Fe-Ge system at 800 °C are listed in Table-3.

The solid solubility ranges of all single-phases in this isothermal section were determined by X-ray diffraction using the phase-disappearing method and comparing the shift of the X-ray diffraction pattern of the samples near the compositions of the binary phases and the ternary phases. In this work, particular interest was given to the evaluation of the homogeneity ranges of the different phases and of their equilibria. The type of structure reported for all the phases have been confirmed.

In the region close to the Fe-Ge sub system, the sample of initial composition $GdFe_{8.4}Ge_{3.6}$ has not been observed as single phase but as an heterogeneous mixture of three phases: a majority substitutional solid solution of germanium in α-iron, $GdFe_2Ge_2$ and Fe_3Ge. Our investigation is in good agreement with the results found by Artigas *et al.* [20] and Lachervre *et al.* [21] but in contrast to Wang *et al.* [22] that proved the existence of the intermetallic $GdFe_{8.4}Ge_{3.6}$ compound.

The ternary compounds based on the $ThMn_{12}$ structure are formed when R and Fe are combined with small amounts of X = Ti, V, Cr, Mo, W, or Si [23-25]. All these compounds can be represented as $ReFe_{12-x}X_x$. The corresponding x values are generally fairly small, but unfortunately are not the same for the various X components [5].

In this work an homogeneity range for the solid solution $GdFe_{12-x}Ge_x$with ($5.7 \leq x \leq 6.3$) has been identified. The composition and the diffraction patterns show a similarity to those of the $Y_{0.5}Co_3Ge_3$ [26].

The ternary compound $Gd(Fe,Ge)_4$ crystallizes with $CeGa_2Al_2$ type of strcture (I4/mmm space group) and has a small homogeneity region up to 5 at %. Francois *et al.* [27] have reported the defected $CeNiSi_2$-type $GdFe_xGe_2$ compound with a wide homogeneity range $0.25 \leq x \leq 0.46$. Our investigations have confirmed this result in this section at 800 °C (Fig. 1). The crystal structure of $GdFe_{0.37}Ge_2$ have been studied by our group [11]. We demonstrated that the variation of x is due to the Fe atom in the (*4c*) crystallogrphic site in this structure that are not fully occupied.

The presence of the $Gd_{117}Fe_{52}Ge_{112}$ compound is characterized by the absence of solid solution. Earlier studies on a series of rare earth $R_{117}Fe_{52}Ge_{112}$ (R = Gd, Dy, Ho, Er, Tm) by Kohlhaas *et al.* [14] described their crystal structures. They have the $Tb_{117}Fe_{52}Ge_{112}$-type structure with a large cubic cell parameter ranging from 28.02(2) to 29.098(6) Å. Nearly isostructural compound $Dy_{117}Co_{57}Sn_{112}$ was also observed [28-30]. The principal distinction between the two structures consist in the fact that in the $Dy_{117}Co_{57}Sn_{112}$ structure the *4b* Wyckoff position (0.5 0.5 0.5) is occupied by Co, whereas in the $Tb_{117}Fe_{52}Ge_{112}$ structure the *4b* site is unfilled.

The magnetic properties of $Gd_{117}Fe_{52}Ge_{112}$ at low temperature have been studied. Fig. 2 shows magnetic susceptibility curve for this compound, in the temperature range 2-300 K. In the paramagnetic state, magnetic susceptibility for this compound follows the Curie-Weiss law and can be then written:

$$\chi = C/(T-\theta p) \qquad (1)$$

where θ is the Curie-Weiss temperature and C is the Curie constant defined as:

$$C = \frac{\mu_0}{3K_B}\mu_{eff}^2 \qquad (2)$$

where $\mu_0 = 4\pi \times 10^{-7}$ H m^{-1} is the permeability, $K_B = 1.38 \times 10^{-23}$ JK^{-1} is the Boltzman constant.

The inverse of the susceptibility $\mu_0H = 2$ KOe as a function of temperature is shown in inset Fig. 2. By fitting the linear paramagnetic of the data in the temperature range 89-300 K, the Curie-Weiss parameters C and θ were obtained. The experimental effective paramagnetic moments, μ_{eff}^{exp}, were calculated from C using the eqn. 2. The temperature range of fit, θ, μ_{eff}^{exp} and μ_{eff}^{cal} per Gd atom [11] are listed in Table-4.

TABLE-3
CRYSTALLOGRAPHIC DATA OF TERNARY Gd-Fe-Ge COMPOUNDS AND SOLID SOLUTIONS STABLE AT 800 °C

Phase	Space group	Structure type	Lattice parameters (Å)			Ref.
			a	b	c	
$GdFe_{0.27}Ge_2$	Cmcm	$CeNiSi_2$	4.1508	16.0609	4.0239	[11]
$GdFe_2Ge_2$	I4/mmm	$CeGa_2Al_2$	3.9950		10.4680	[12]
$GdFe_6Ge_6$	P6/mmm	YCo_6Ge_6	5.1280		4.0760	[13]
$Gd_{117}Fe_{52}Ge_{112}$	Fm-3m	$Tb_{117}Fe_{52}Ge_{112}$	28.710			[27]

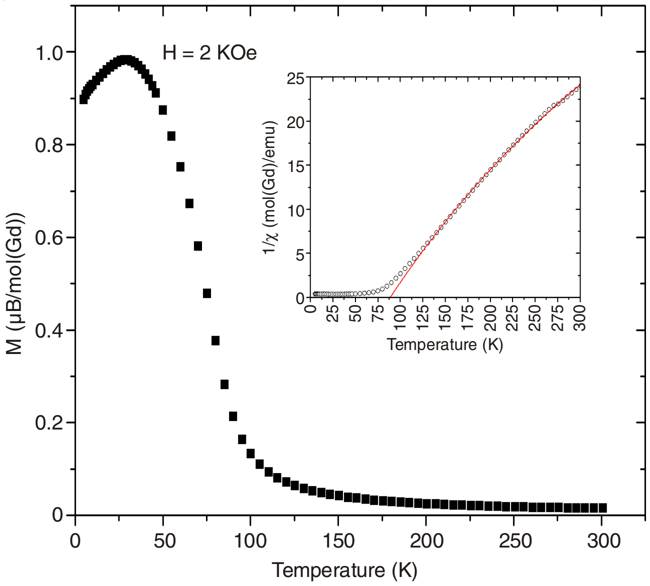

Fig. 2. Magnetization of $Gd_{117}Fe_{52}Ge_{112}$ measured as a function of temperature in a 2 KOe applied magnetic field. The inset shows the curie-weiss fit of the linear part of the reciprocal susceptibility

TABLE-4
C, θ, μ_{eff}^{exp} AND μ_{eff}^{cal} VALUES FOR $Gd_{117}Fe_{52}Ge_{112}$ COMPOUND

Compound	$C_{(EMUK/mol)}$	Θ (K)	μ_{eff}^{exp} (μ_B)	μ_{eff}^{cal} (μ_B)
$Gd_{117}Fe_{52}Ge_{112}$	6.481	89	7.2	7.94

The value of μ_{eff}^{exp} (μ_B) is slightly smaller than the theoretical effective paramagnetic moment from the Russell-Saunders coupling for The trivalent Gd ($g_J[J(J+1)]^{1/2} = 7.94\ \mu_B$. This suggest that in this compound Fe atoms do not carry localized magnetic moment. The lowering of the μ_{eff}^{cal} value for Gd atoms indicates the presence of crystal field effect or possible non-collinearity of magnetic structure or both. This agree with the similar results observed for $Gd_{117}Co_{56.4}Sn_{114.3}$ and $Tb_{117}Co_{58}Sn_{112}$ [31].

The temperature dependence of the magnetic susceptibility indicates a magnetic phase transition below 89 K for this compound. At lower temperatures, a deviation from the curie weiss law was observed and suggested onset of a ferromagnetic magnetic ordering.

The phase relation and the number of the ternary compounds found in the Gd-Fe-Ge system at 800 °C make it very similar with other systems as known from literature Tb, Dy, Ho, Er, Tm [7]. Isostructural intermetallic compounds occuring in all R-Fe-Ge systems, including those for which the isothermal sections were not constructed, are presented in Table-5. Analysis of the series of ternery compounds in the R-Fe-Ge systems show that the $RFeGe_3$ ($BaNiSn_3$-type of structure), $RFe_{0.67}Ge_{1.33}$ (AlB_2-type of structure), $R_9Fe_{10}Ge_{10}$ ($Tm_9Fe_{10}Ge_{10}$-type of structure), $R_3Fe_2Ge_3$ ($Hf_3Ni_2Si_3$-type of structure) and the $R_4Fe_3Ge_4$ ($CeNiSi_2$-type of structure) compositions are typical for the light rare earth containing systems. Oppositely, the RFe_xGe ($CeNiSi_2$-type of structure), the RFe_2Ge_2 ($CeAl_2Ga_2$-type of structure), the RFe_6Ge_6 (YCo_6Ce_6-type of structure) and the RFe_4Ge_2 ($ZrFe_4Si_2$-type of structure) compounds are typical for heavy rare-earth intermetallic systems. The series of RFe_xGe_2, RFe_2Ge_2 and $Tb_{117}Fe_{52}Ge_{112}$ intermetallics combine with all the rare-earth elements. Finally, only four new ternary compounds crystallizing with the $Tm_9Fe_{10}Ge_{10,}$ W_3CoB_3 and $Hf_3Ni_2Si_3$ structure types were found in the Er-Fe-Ge.

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TABLE-5
ISOTYPIC SERIES OF THE TERNARY R-Fe-Ge COMPOUNDS

Composition	Structure type		La	Ce	Pr	Nd	Sm	Eu	Y	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
RFe_xGe_2	$CeNiSi_2$	oS16, 63	+	+	+	+	+	–	+	+	+	+	+	+	+	+	+
RFe_6Ge_6	$Y_{0.5}Co_3Ge_3$	hP8, 19	–	–	+	+	+	–	+	+	+	+	+	+	+	+	+
RFe_2Ge_2	$CeAl_2Ga_2$	tI10, 139	+	+	+	+	+	–	–	+	+	+	+	+	+	+	+
RFe_4Ge_2	$ZrFe_4Si_2$	tP14, 136	–	–	–	–	–	–	+	–	+	+	+	+	+	+	+
$RFeGe_3$	$BaNiSn_3$	tT10, 107	–	+	+	–	–	–	–	–	–	–	–	–	–	–	–
$R_{117}Fe_{52}Ge_{112}$	$Tb_{117}Fe_{52}Ge_{112}$	cF11241, 225	–	–	+	–	+	–	–	+	+	+	+	+	+	–	–
$R_4Fe_{0.85}Ge_7$	$Sm_4Co_{0.64}Ge_7$	oS24, 38	–	–	+	–	–	–	–	–	–	–	–	–	–	–	–
$R_6Fe_{13}Ge$	$PrFe_{23}$	tI30, 140	–	–	+	–	–	–	–	–	–	–	–	–	–	–	–
$RFe_{0.67}Ge_{1.33}$	AlB_2	hP3, 191	+	–	–	+	+	–	–	–	–	–	–	–	–	–	–
R_5FeGe_3	$CuHf_5Sn_3$	hP18, 193	+	–	–	–	–	–	–	–	–	–	–	–	–	–	–
$R_{15}FeGe_9$	$La_{15}FeGe_9$	hP50, 186	+	–	–	–	–	–	–	–	–	–	–	–	–	–	–
$R_4Fe_{0.64}Ge_7$	$Sm_4Co_{0.64}Ge_7$	oS24, 38	–	–	–	+	–	–	–	–	–	–	–	–	–	–	–
R_6FeGe_{13}	$La_6Co(Co_{0.5}Ga_{0.5})_4$	tI80, 140	–	–	–	+	–	–	–	–	–	–	–	–	–	–	–
$R_{0.45}Fe_3Ge_{3.1}$	$Cu_{5.44}Tb_{0.78}$	hP8, 191	–	–	–	–	+	–	–	–	–	–	–	–	–	–	–
$RFe_{0.38}Ge_{4.21}$	Mg_3EuGe_3	oS28, 63	–	–	–	–	+	–	–	–	–	–	–	–	–	–	–
$R_9Fe_{10}Ge_{10}$	$Tm_9Fe_{10}Ge_{10}$	oI58, 71	–	–	–	–	–	–	–	–	–	–	–	+	+	–	–
R_3FeGe_3	W_3CoB_3	oS28, 63	–	–	–	–	–	–	–	–	–	–	–	+	–	–	–
$R_3Fe_2Ge_3$	$Hf_3Ni_2Si_3$	oS32, 63	–	–	–	–	–	–	–	–	–	–	–	+	+	–	–
$R_4Fe_3Ge_4$	$CeNiSi_2$	oI22, 71	–	–	–	–	–	–	–	–	–	–	–	+	+	–	–
RFeGe	YbFeGe	mS12, 12	–	–	–	–	–	–	–	–	–	–	–	–	–	+	–

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