第15卷 第2,3期 广东有色金属学报 Vol. 15, No. 2,3
2005年9月 JOURNAL OF GUANGDONG NON-FERROUS METALS Sep 2005

Article ID: 1003-7837(2005)02,03-0074-08

Structure and physical properties of high pressure phases in rare earth intermetallic systems $R(Fe_{1-x}M_x)_2$ and $R'_{1-x}R''_xFe_2$

Ilyushin A. S.

(Lomonosov Moscow State University, Russia 119992, Moscow)

CLC number: TG115, TG146.45 Document code: A

1 Introduction

Rare earth intermetallic compounds of Laves phases stoichiometry RT_2 are crystallized in two structural types: hexagonal C14 and cubic C15. For long time they have been a subject of particular interest in solid state physics [1-6]. Two main reasons were for this attention: (1) Scries RT_2 were very good physical models for wide theoretical and experimental study of this kind of materials; (2) many of these compounds and alloys demonstrate extraordinary magnetic properties, for example, giant magnetostriction and giant magnetic anisotropy which are opening wide perspectives for their practical usages.

These objects are active absorbents of hydrogen, so there are studying their hydrogen absorption [5].

Unfortunately, not all rare earth elements can organize Laves phases C14 and C15 at ordinary conditions of synthesis. Nevertheless this goal can be achieved by using of high pressure crystallization (8 GPa). This method was designed in the Institute of High Pressures Physics of Russian Academy of Sciences. It was developed by Dr. A. Tsvyaschenko [7-9]. In cooperation with his laboratory we have synthesized intermetallic compounds of rare earth and 3d-transition metals and also alloys of pseudobinary systems on their base. Even more, using this unique method of fabrication we have had possibilities to produce intermetallic compounds with the same chemical composition in two different structural modifications, i. e. to make "artificial" polymorphism. In this report we are delivering our results concerning fabrications of high pressure phases in intermetallic compounds of stoichiometry RT_2 and in alloys of pseudobinary systems on their base like $R'_{1-x}R_x"T_2$ and $R(T'_{1-x}T"_x)_2$ crystallized in structural types of Laves phases with cubic C15 and hexagonal C14 unit cells (Fig. 1).

Both structures C14 and C15 are similar each other in respect of atomic coordination and can be considered as two-sublattice system of R- and T-atoms.

We have had the following goals: (1)synthesis of high pressure phases; (2)study of their phase composition, definition of atomic crystal structures and parameters of unit cells; (3)study of their magnetic and sorption properties; (4)building of phase diagrams for pseudobinary systems in coordinates "composition-

Received date: 2005-08-29

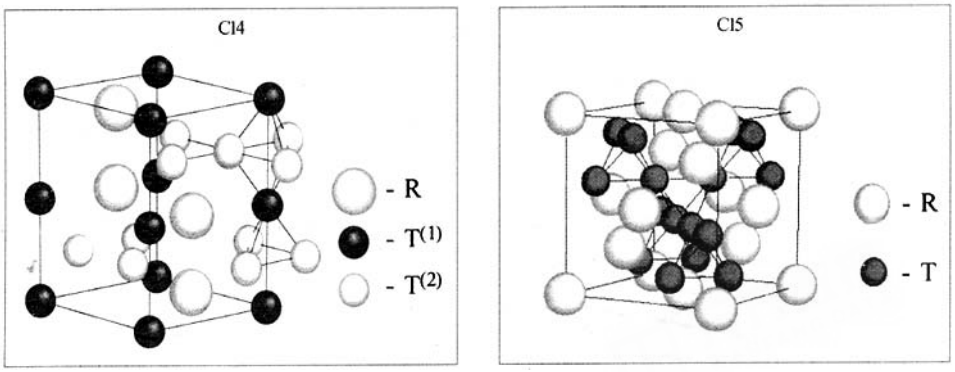

Fig. 1 Unit cells of hexagonal C14 and cubic C15 Laves phases

pressure".

We have used as experimental methods: (1)X-ray diffractometry of polycrystals; (2)Magnetic measurements; (3)M ssbauer spectroscopy. Experimental details could be found in [1, 9-11].

2 Structure and magnetic properties of intermetallic compounds RT_2

After synthesis under pressure 8GPa we could fabricate intermetallic compounds $YbFe_2$, $NdFe_2$, $NdCo_2$, $NdNi_2$, crystallized in structural type of cubic Laves phase C15 and intermetallic compounds $YbMn_2$, $ErMn_2$, $HoMn_2$, $DyMn_2$ and $TbMn_2$ crystallized in structural type of hexagonal Laves phase C14 as well as pseudobinary systems of alloys on their base: $Er_{1-x}Tb_xMn_2$, $Ho_{1-x}Tb_xMn_2$, $Dy(Fe_{1-x}Mn_x)_2$, $Tb(Fe_{1-x}Mn_x)_2$, $Yb(Fe_{1-x}Mn_x)_2$, $Nd(Fe_{1-x}Mn_x)_2$, $Yb(Fe_{1-x}Al_x)_2$, $Nd(Fe_{1-x}Co_x)_2$, $Nd(Fe_{1-x}Ni_x)_2$.

Data concerning structure and temperatures of magnetic ordering is listed in Table 1.

Table 1 Crystallographic and magnetic characteristics of intermetallics RT_2

RT_2	Structure	a/Å	c/Å	$V_{f.u.}$/Å^3	T_c/K
$ErMn_2$	C14	5.273	8.632	51.72	25
$HoMn_2$	C15	7.519	—	53.06	26
$HoMn_2$	C14	5.316	8.672	53.05	27
$DyMn_2$	C15	7.553	—	53.94	39
$DyMn_2$	C14	5.346	8.733	53.96	37
$TbMn_2$	C15	7.577	—	54.37	40
$TbMn_2$	C14	5.349	8.779	54.38	43
$YbMn_2$	C14	5.230	8.513	50.42	—
$YbFe_2$	C15	7.245	—	47.54	541
$NdFe_2$	C15	7.447	—	51.62	563
$NdCo_2$	C15	7.309	—	48.81	90
$NdNi_2$	C15	7.225	—	47.14	16

3 Phase diagrams of pseudobinary systems $Er_{1-x}Tb_xMn_2$ and $Tb_{1-x}Ho_xMn_2$

Alloys of pseudobinary systems $Er_{1-x}Tb_xMn_2$ and $Tb_{1-x}Ho_xMn_2$ have been synthesized under normal

pressure and under pressures 1, 2, 3, 4, 5, 6 and 8 GPa.

According to data of X-ray analysis of synthesized alloys in systems can be formed either single phase structures C14 or C15 or two-phase regions with mixture of C14 and C15. It depends on composition and pressure of synthesis. Phase diagrams of the systems $Er_{1-x}Tb_xMn_2$ and $Tb_{1-x}Ho_xMn_2$ in coordinates "composition-pressure" are shown in Fig. 2.

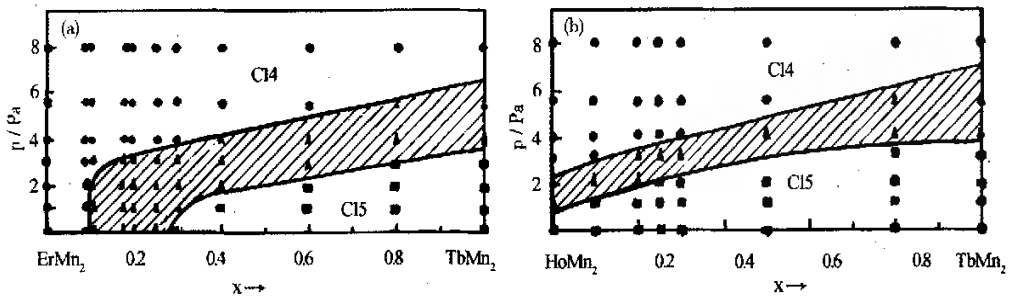

Fig. 2 Phase diagrams of pseudobinary systems $Er_{1-x}Tb_xMn_2$ (a) and $Tb_{1-x}Ho_xMn_2$ (b)

From the Fig. 2 it can be seen that in the system $Er_{1-x}Tb_xMn_2$ at pressures higher than 6 GPa alloys of all compositions $0<x<1$ are isotypic to hexagonal Laves phase C14 and are organizing continual series of solid solution of Er and Tb atoms in R-sublattice of structure C14.

The region of alloys which are isotypic to cubic Laves phase C15 is limited by the composition and by pressure. It can be found at concentration Tb $x = 0, 3$ at normal pressure. If the pressure becomes higher then this region shrinks. Single phase regions with structures C14 and C15 are divided from each other by the mixture of two-phases C14+C15.

In the system $Tb_{1-x}Ho_xMn_2$ at low pressure there is continual series of solid solutions of atoms Ho and atoms Tb in R-sublattice of cubic Laves phase C15. At high pressures continual series of solid solutions are forming in R-sublattice of hexagonal Laves phase C14 in whole range of composition $0<x<1$.

4 Phase diagrams of pseudobinary systems $Dy(Fe_{1-x}Mn_x)_2$, $Tb(Fe_{1-x}Mn_x)_2$ and $Yb(Fe_{1-x}Mn_x)_2$

Alloys of pseudobinary systems $Dy(Fe_{1-x}Mn_x)_2$ and $Tb(Fe_{1-x}Mn_x)_2$ were synthesized under the pressures up to 8 GPa. Phase diagrams of pseudobinary systems $Dy(Fe_{1-x}Mn_x)_2$ and $Tb(Fe_{1-x}Mn_x)_2$ are shown on the Fig. 3.

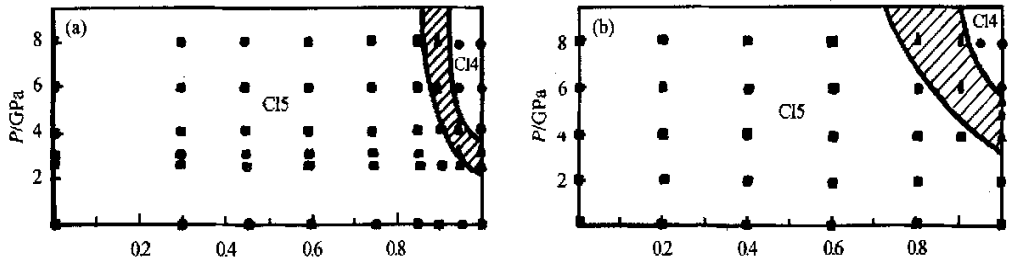

Fig. 3 Phase diagrams of pseudo-binary systems $Dy(Fe_{1-x}Mn_x)_2$ (a) and $Tb(Fe_{1-x}Mn_x)_2$ (b)

From the Fig. 3 it can be seen that in the system $Dy(Fe_{1-x}Mn_x)_2$ under pressures less than 2 GPa in whole range of concentrations $0<x<1$ all alloys are single phase with structure C15. Fe and Mn atoms are

forming continual series of solid solutions in 3d-sublattice of C15.

At higher pressure in the region enriched by Mn ($0.08< x <1$) in the system are forming hexagonal Laves phase C14. It divided from the region of cubic phase C15 by the two-phase region C14+C15.

Phase diagram of pseudo-binary system $Tb(Fe_{1-x}Mn_x)_2$ is similar to phase diagram of pseudo-binary system $Dy(Fe_{1-x}Mn_x)_2$.

From these phase diagrams it can be seen that in both systems in regions with high concentration of Mn at high pressure hexagonal phases C14 exist. It means that we have gotten artificial polymorphism.

Phase diagram of pseudo-binary system $Yb(Fe_{1-x}Mn_x)_2$ is shown in the Fig. 4.

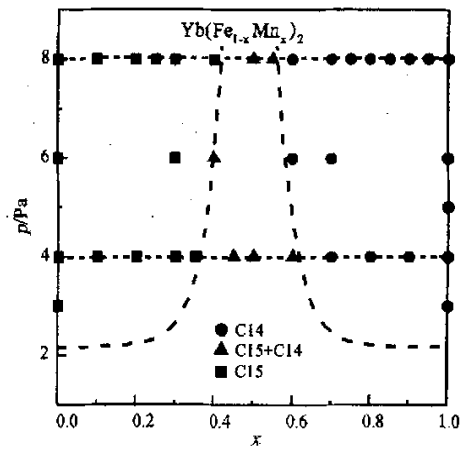

Fig. 4 Phase diagram of pseudo-binary system $Yb(Fe_{1-x}Mn_x)_2$

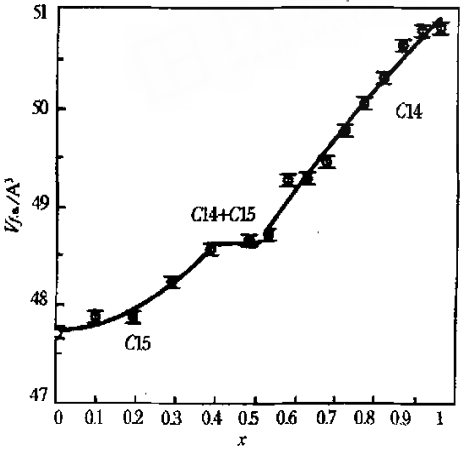

Fig. 5 The concentration curve $V_{f.u.}$ for the system $Yb(Fe_{1-x}Mn_x)_2$

In this system we also have limited regions of phases C14 and C15 divided by the region of their mixture C14+C15.

On the Fig. 5 it is presented the curve of dependence of volume $V_{f.u.}$ from the concentration x in pseudo-binary system $Yb(Fe_{1-x}Mn_x)_2$ synthesized under pressure 8GPa.

It can be seen that substitution of Fe atoms by Mn atoms leads to monotonous but non-linear growth of $V_{f.u.}$ with "plato" corresponding two-phase region. The same dependences demonstrated alloys of systems $Dy(Fe_{1-x}Mn_x)_2$ and $Tb(Fe_{1-x}Mn_x)_2$.

5 The structure and crystal characteristics of alloys in pseudo binary systems $Nd(Fe_{1-x}Co_x)_2$, $Nd(Fe_{1-x}Ni_x)_2$, $Nd(Fe_{1-x}Mn_x)_2$, $Yb(Fe_{1-x}Al_x)_2$ synthesized under the pressure 8 GPa

Alloys of pseudo-binary systems $Nd(Fe_{1-x}Co_x)_2$, $Nd(Fe_{1-x}Ni_x)_2$, $Nd(Fe_{1-x}Mn_x)_2$, $Yb(Fe_{1-x}Al_x)_2$ with structures of Laves phases C14-C15 were synthesized only under the pressure 8 GPa.

According to X-ray studies in the systems $Nd(Fe_{1-x}Co_x)_2$ and $Nd(Fe_{1-x}Ni_x)_2$ we could get single phase samples with structure C15 in whole range of concentration $0\leq x \leq 1$.

In the system $Nd(Fe_{1-x}Mn_x)_2$ cubic Laves phase C15 we could get under the pressure 8 GPa only for the concentrations $0\leq 0.5\leq 1$.

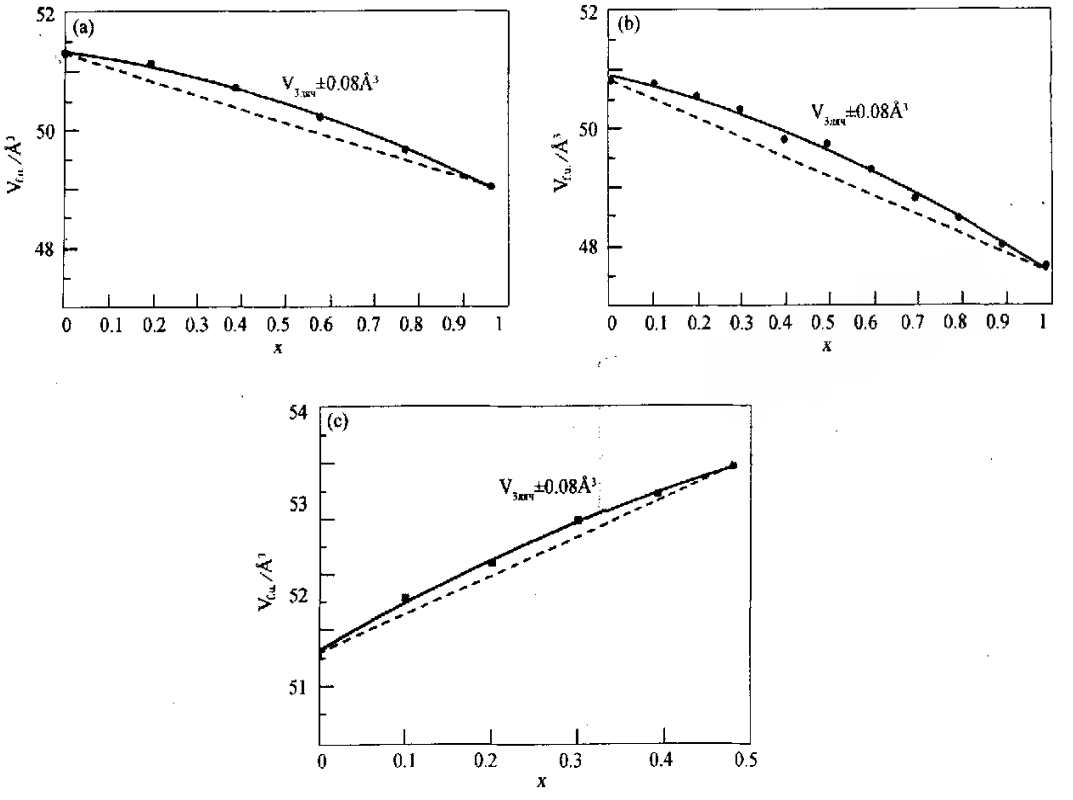

Fig. 6 The concentration curve $V_{f.u.}$ for the systems $Nd(Fe_{1-x}Co_x)_2$ (a), $Nd(Fe_{1-x}Ni_x)_2$ (b) and $Nd(Fe_{1-x}Mn_x)_2$ (c)

Curves for volume $V_{f.u.}$ vs concentration x for systems $Nd(Fe_{1-x}Co_x)_2$, $Nd(Fe_{1-x}Ni_x)_2$ and $Nd(Fe_{1-x}Mn_x)_2$ are shown on the Fig. 6. It can be seen that with the growth of concentration of Co or Ni component in the systems $Nd(Fe_{1-x}Co_x)_2$ and $Nd(Fe_{1-x}Ni_x)_2$ volume $V_{f.u.}$ monotonously decreases. In the system Nd $(Fe_{1-x}Mn_x)_2$ with the growth of concentration of Mn the volume $V_{f.u.}$ monotonously increases. So, it is possible to modify inter-atomic distances and inter-atomic interactions by the combination of different metals in multi-component Laves phases.

The situation is more complicated in the system $Yb(Fe_{1-x}Al_x)_2$. The synthsis under pressure 8 GPa provided the fabrication of intermetallic compounds $YbFe_2$ and $YbAl_2$ with cubic structures C15. But in alloys with intermediate constitutions the region of solid solution of Al in 3d-sublattice of $YbFe_2$ exists only up to $x = 0.3$. It means that Al atoms can substitute only 30% of Fe atoms. In turn, Fe atoms can substitute in 3d-sublattice of intermetallic $YbAl_2$ only 25% of Al atoms.

In the middle region of concentration $0.40 \leq x \leq 0.65$ in the system $Yb(Fe_{1-x}Al_x)_2$ the new phase with hexagonal structure C14 is formed. It divided from the Laves phases C15 by the two-phase regions.

On the Fig. 7 it is shown the concentration curve $V_{f.u.}$ for the system $Yb(Fe_{1-x}Al_x)_2$. It can be seen that volume $V_{f.u.}$ grows from 47.53 Å³ to 61.14 Å³, forming two "platos", corresponding two-phases regions. We can conclude that the high pressure synthesis provides solution some problems of metal physics: (1) forming of new polymorphic crystal modifications in well-known intermetalllic compounds RT_2: hexagonal high pressure phases C14 in cubic Laves phases C15 $HoMn_2$, $DyMn_2$, $TbMn_2$ and others; (2) forming of Laves phases in rare earth termetallics RT_2 with R = Yb and Nd: $YbFe_2$, $YbMn_2$, $NdFe_2$, $NdCo_2$, $NdNi_2$; (3) forming on base of new or polymorphic modifications of intermetallics RT_2 pseudo-binary systems

like as $R'_{1-x}R_x''T_2$ and $R(T'_{1-x}T''_x)_2$, providing to modify structural parameters and physical and chemical properties of these materials. We will give some examples of the using of these possibilities.

6 Sorption and magnetic properties of intermetallic alloys

We have studied the sorption of hydrogen and deuterium by the alloy $Dy(Fe_{0.05}Mn_{0.95})_2$, crystallized in two polymorphic modifications C14 and C15.

According to X-ray data the alloy $Dy(Fe_{0.05}Mn_{0.95})_2$ synthesized under normal pressure has the cubic structure C15 with parameters: $a = 7.536$ Å and $V_{f.u.} = 53.5$ Å^3.

The same alloy synthesized under the pressure 8 GPa has the hexagonal structure C14 with parameters: $a = 5.319$ Å, $c = 8.692$ Å and $V_{f.u.} = 53.2$ Å^3.

After introducing of H and D in samples of alloy $Dy(Fe_{0.05}Mn_{0.95})_2$ were found their structural crystal parameters and amount of quantities of H and D. Experimental data are shown in Table. 2.

From the data of Table. 2 we can see that sorption of H and D by the alloys in two modifications C14 and C15 lead to growth of volume $V_{f.u.}$ more than 20%. In hexagonal modification H and D are incorporating less active than in cubic modification, but absorption of H in both cases is higher than absorption of D.

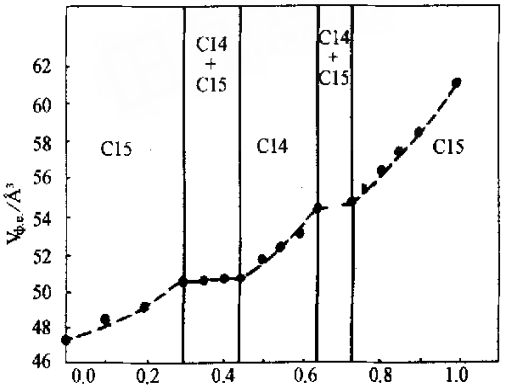

Fig. 7 The concentration curve $V_{f.u.}$ for the system $Yb(Fe_{1-x}Al_x)_2$

Table 2 Number of atoms H and D and dilatation $\Delta V/V$ on formula unit of alloys $Dy(Fe_{0.05}Mn_{0.95})_2X_n$ (X - H or D)

Structure	X	n	$\Delta V/V$, %
C14	H	4.1(2)	23(2)
C15	H	4.6(2)	28(2)
C14	D	3.2(2)	21(2)
C15	D	3.8(2)	25(2)

Mossbauer spectra of polymorphic modifications and their deuterids for alloy $Dy(Fe_{0.05}Mn_{0.95})_2$ are shown on the Fig. 8.

According to the calculation of M ssbauer spectra for $Dy(Fe_{0.05}Mn_{0.95})_2D_n$ there are additional doublets. They relate with organizing of groups "3d-metal-deuterium". Relative intensity of this additional doublet in spectrum of alloy $Dy(Fe_{0.05}Mn_{0.95})_2D_n$ with the structure C15 is higher than relative intensity of additional doublet in spectrum of alloy $Dy(Fe_{0.05}Mn_{0.95})_2D_n$ with the structure C14. It means that sorption of deuterium by hexagonal phase C14 less than cubic phase C15. It can be explained by using of crystallographic point of view. Fe atoms in structure C14 occupy only one of two non-equivalent positions-$T^{(2)}$. Mn atoms occupy the positions $T^{(1)}$. Deuterium atoms concentrate near the Mn atoms, so sorption of D atoms in C14 less than C15.

The second sample is concerning the magnetic properties of the system $Yb(Fe_{1-x}Mn_x)_2$. It is known [10] that intermetallic compound $YbFe_2$ has point of magnetic compensation on the curve "magnetization vs

temperature". It means that $YbFe_2$ has ferromagnetic structure.

We studied field dependences of magnetization for alloys of system $Yb(Fe_{1-x}Mn_x)_2$ for $0 \leq x \leq 0,4$. Curves of these measurements are shown on the Fig. 9. It was done at room temperature for $X=0.1, 0.15, 0.2, 0.3, 0.4$.

It is easy to see that all curves demonstrates the typical behavior except for $x=0.2$. Much more clear it can be seen on curve $M_{f.u.}$ vs concentration where anomaly like λ−point is present (Fig. 9, cut−off).

More essential anomalies demonstrate curves of temperature dependences for $M_{f.u.}$ (Fig. 10). We can see on those curves points of compensation.

We have found that points of magnetic compensation T_{comp} in alloys of the system $Yb(Fe_{1-x}Mn_x)_2$ depends on composition by very complicated way and curve of concentration dependence for T_{comp} demonstrates anomaly like positive λ-point (Fig. 11).

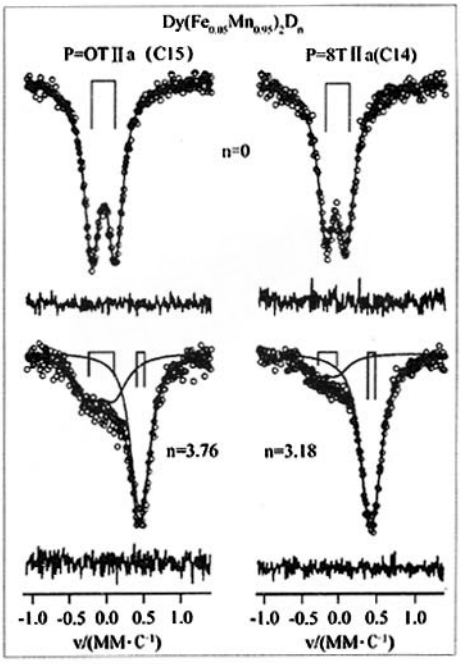

Fig. 8 M ssbauer spectra of polymorphic modifications C14 and C15 and their deuterids for alloy Dy $(Fe_{0.05}Mn_{0.95})_2$

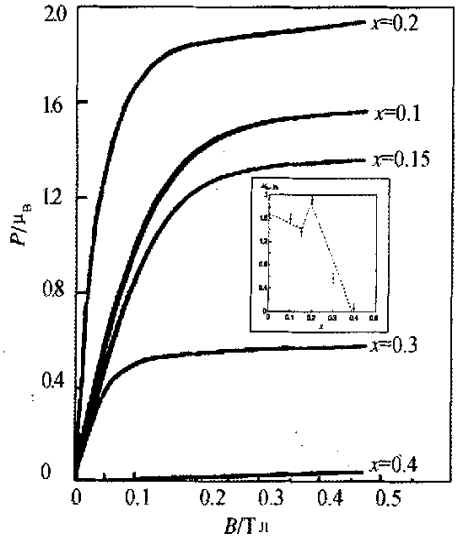

Fig. 9 Field dependences of magnetization for alloys of system $Yb(Fe_{1-x}Mn_x)_2$ (cut-off: dependence magnetic moment $M_{f.u.}$ vs concentration)

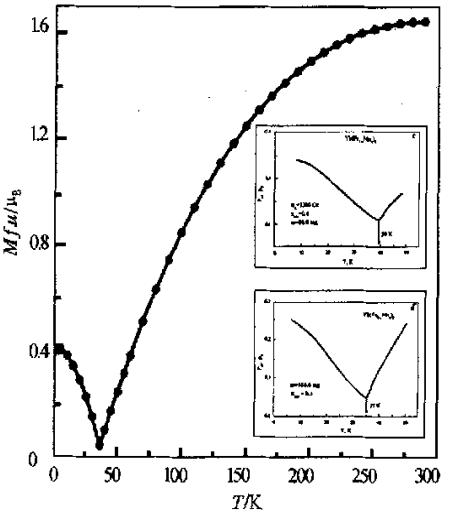

Fig. 10 Curves of temperature dependences for magnetic moment $M_{f.u.}$ for $YbFe_2$ (cut-off - fragments of curves for $M_{f.u.}(T)$ for $x = 0.3$ and 0.4)

We have concluded that there are not simple ferrimagnetic structure in alloys of system $Yb(Fe_{1-x}Mn_x)_2$ with $x > 0.1$. Alloys with $x = 0.1$ may have ferrimagnetic structure and Mn can be considered as simple non-magnetic solvent. More higher concentration of Mn leads to the forming of different local arrangements and changes the character of magnetic interactions. So in this case simple ferrimagnetic model is unacceptable for analysis of concentration dependences for compensation points[11].

We can conclude that high pressure synthesis of alloys provides the wide perspectives to creation of new materials.

The author thanks his colleagues doctors: Tsvyaschenko A. V., Nikanorova I. A., Spazhakin I. V., Al Dervish M., Persikova I. A., Fomicheva L. A. and professor Rusakov V. S.

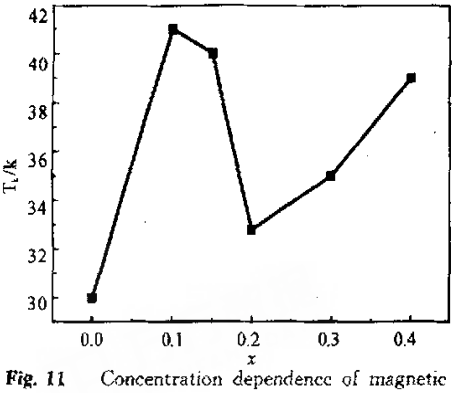

Fig. 11 Concentration dependence of magnetic compensation temperature for system $Yb(Fe_{1-x}Mn_x)_2$

References

[1] Ilyushin A S. Introduction in structural physics of Rare EarthIntermetallic compounds. M. MSU. 1991.

[2] Taylor K N R. Intermetallic Rare-Earth compounds. M. "Mir". 1974.

[3] Wallace W. E. Rare earth intermetallics. N-Y, London, Academic Press. 1973.

[4] Belov K P. Rare Earth magnetics and their usages. M. "Nauka". 1980.

[5] Hydrogen in Metals. Basic properties. Springer-Verlag. Berlin Heidelberg, N-Y. 1978.

[6] Belov K P. Magnetostriction and its technical applies. M. "Nauka". 1987.

[7] Strong G. High temperature methods at high pressures. M. "Mir". 1964.

[8] Shinjaev A. Phase transformations and properties of alloys at high pressure. M. "Nauka". 1973.

[9] Khvostantsev L G., Vereshchagin L F, Novikov A P. High temp.-high press., 9, p637-639, 1977.

[10] Inoue K, Nakamura Y, Tsvyaschenko A V, Fomicheva L J, Magn. And Magn. Materials, 140-144, p. 797-798, 1995.

[11] Ilyushin A S, Nikanorova I. A., Tsvyaschenko A V, et al. Vestnik Moskovskogo universiteta. Physics. Astronomy. 2004, No. 2, p51-54.