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Structural and Magnetic Phase Transitions in High Pressure Laves Phases $R(Fe_{1-x}M_x)_2$

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***Abstract* – The paper presents the results of study of structural and magnetic properties of alloys of quasi-binary systems $R(Fe_{1-x}M_x)_2$, where R is REE and M is 3d-metal. It is shown that synthesis under extreme conditions, i.e. high temperatures and high pressures makes it possible to obtain alloys with the Laves phase structure, which cannot be obtained under normal synthesis. These are alloys with rare earth elements Yb, Nd and Pr. For all systems studied the structural and magnetic phase diagrams are determined. The areas of single-phase patterns are determined. It is shown that structural phase transitions occur through the morphotropic region, where two Laves phases coexist, i.e. cubic C15 and hexagonal C14 phases. In addition the temperatures of magnetic order-disorder phase transitions (Curie temperatures) are determined for these systems. For the system of alloys $Pr(Fe_{1-x}Al_x)_2$ these values are compared with the data obtained from Mossbauer studies of temperature.**

Keywords – laves phases; phase transition; Curie temperature; magnetostriction.

I. INTRODUCTION

The intermetallic compounds of rare-earth metals are widely used in science and technology due to their outstanding physical and magnetic properties. In this class of compounds, a special place in connection with the search for new magnetic materials is occupied by intermetallic compounds of rare-earth metals with 3d-transition metals (Fe, Co, Ni, Mn), in particular, compounds of the RM_2 type with the Laves phase structure. The stoichiometry RM_2 is found in two structural types: the cubic C15 Laves phase and the hexagonal C14 Laves phase [1,2].

On the one hand, due to the peculiar crystallographic and magnetic structures, these compounds are convenient model objects for studying a number of fundamental problems of modern condensed matter physics, including the establishment of relationship between electronic characteristics of atoms or ions that make up a solid and its physical properties [3]. One of the methods used for solving this problem is systematic study of structural phase transitions as well as determination of their physical nature. The Laves phases allow a comprehensive theoretical and experimental study of the laws of structural phase transitions during magnetic ordering, and a "giant" magnitude of spontaneous magnetostriction allows quantitative measurements of distortions of atomic and crystalline structure. The study of quasi-binary systems makes it possible to study "spin reorientation" and its influence on distortion phase transitions.

Therefore, the systematic study of both structural and magnetic phase transitions is an urgent task for physics of magnetic phenomena, physics of the condensed state of matter, physical chemistry, and materials science. This circumstance makes it necessary to synthesize and investigate quasi-binary, quasi-transnational and more complex systems based on rare-earth compounds with the Laves phases structures in order to form new magnetic materials with a given set of optimal physicochemical characteristics. In this regard, one of the important areas of physics of rare-earth intermetallic compounds is the synthesis of new alloys and the study of structural and magnetic phase transitions.

It should be noted that there are a number of rare-earth elements (ytterbium Yb, neodymium Nd, praseodymium Pr) with which it is impossible to obtain intermetallic compounds of the Laves phase of RM2 type under normal synthesis conditions. Therefore, synthesis is used under extreme conditions, i.e. high pressures and high temperatures. Synthesis under extreme conditions makes it possible to obtain alloys of quasi-binary systems, which cannot be obtained under ordinary conditions of synthesis, to obtain intermetallic compounds of the same composition in two different crystal and structural modifications, i.e. to create an "artificial" polymorphism. Thus, when combining the composition of multicomponent Laves phases, one can vary the interatomic distance, and, consequently, the nature of interatomic exchange interactions leading to one or another type of magnetic ordering.

The purpose of this work was to synthesize high pressure phases of alloys of quasi-binary systems $R(Fe_{1-x}M_x)_2$ (R is REE and M is 3d-metal) which are isotype to the C14 and C15 Laves phases. Another purpose was to study the influence of substitution of magnetic atoms in the 3d sublattice with non-magnetic or magnetic atoms on the atomic and crystalline structure, the nature of structural and magnetic phase

transitions, as well as influence on the exchange interaction, leading to one or another type of magnetic ordering.

II. METHODS AND MATERIALS

This paper presents the results of studies of the structure, phase composition, magnetic properties and hyperfine interactions of a wide spectrum of rare-earth intermetallic compounds and alloys on their basis, which were synthesized at high pressures: $Y(Fe_{1-x}Al_x)_2$, $Yb(Fe_{1-x}Al_x)_2$, $Pr(Fe_{1-x}Al_x)_2$, $Nd(Fe_{1-x}Al_x)_2$, $Yb(Fe_{1-x}Mn_x)_2$, $Ho(Fe_{1-x}Mn_x)_2$, $Tb(Fe_{1-x}Mn_x)_2$, $Dy(Fe_{1-x}Mn_x)_2$, $Nd(Fe_{1-x}Co_x)_2$, $Nd(Fe_{1-x}Ni_x)_2$, $Nd(Fe_{1-x}Mn_x)_2$.

All alloys that are high pressure phases were obtained at high pressures from 3 to 8 GPa in a toroid-type chamber designed at the Institute of High Pressure Physics, Russian Academy of Sciences, Ph.D. in Physical and Mathematical Sciences, A.V. Tsvyaschenko [4].

The following research methods were used:

- X-ray diffractometry of polycrystals;
- Measurements of magnetization of alloys in fields up to 15 kOe in a wide temperature range using a pendulum magnetometer (Dominicali type);
- Mossbauer spectroscopy ranging from nitrogen to room temperature;
- Measurements of magnetostriction by tensometric method.

The error in measuring the specific magnetization did not exceed 5% and magnetostriction did not go higher than 6%.

III. RESULTS

A. Structure and magnetic properties of quasi-binary alloys systems $R(Fe_{1-x}Al_x)_2$

In this system of alloys, the substitution in the 3d sublattice of iron atoms by aluminum atoms was made. It is known that Al has an empty 3d zone (electron configuration is $3d^0$) and its replacement with iron atoms allows observing dilution effects in alloys of the systems $R(Fe_{1-x}Al_x)_2$, where R = Y, Yb, Pr, Nd.

The X-ray structural analysis showed that in the Y(Fe1-xAlx)2 system the isomorphic substitution of iron atoms by aluminum atoms is possible only in a limited region of aluminum concentration x = 0 ÷ 0.2. In this region the alloys were synthesized and studied with the following substitution parameter x = 0; 0.05, 0.1, 0.15 and 0.2. The alloys of the Yb (Fe1-xAlx) 2 system were synthesized with the following compositions: x = 0, 0.1, 0.2, 0.3, 0.35, 0.4, 0.45, 0.5, 0.55, 0.6, 0.65, 0.7, 0.75, 0.8, 0.85, 0.9, 1.0. The $Pr(Fe_{1-x}Al_x)_2$ and $Nd(Fe_{1-x}Al_x)_2$ alloys were prepared with a step of 0.1 in the entire substitution region x = 0 ÷ 1.0.

Using X-ray analysis, it was found that in the range of indicated aluminum concentrations, all $R(Fe_{1-x}Al_x)_2$ alloys are single-phase, and all the starting compounds (x = 0) are isotype to the cubic C15 Laves phase. With an increase in the aluminum concentration in all systems, with the exception of the Y(Fe1-xAlx)$_2$ alloy system, structural phase transformations are observed with the formation of two-phase regions in the region of intermediate aluminum concentrations [5, 6]. Figure 1 shows the structural phase diagram of alloys of the $Nd(Fe_{1-x}Al_x)_2$ system.

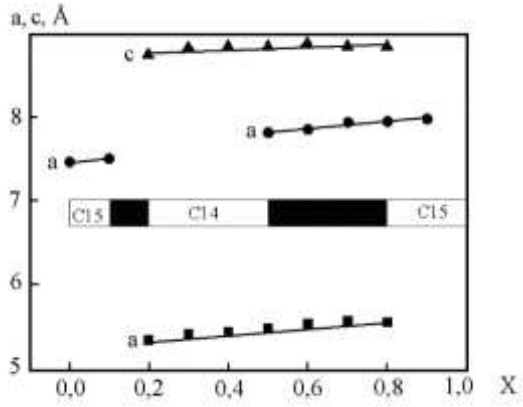

Fig. 1. Diagram of phase composition of system alloys $Nd(Fe_{1-x}Al_x)_2$ and unit cell parameters in the concentration range x = 0 ÷ 1.

It has been established that in the concentration range of $0 \le x \le 0.1$ the $Nd(Fe_{1-x}Al_x)_2$ alloys have a C15 cubic structure. In the area of aluminum concentrations $0.2 < x < 0.5$, the diffraction patterns of alloys contain reflections characteristic of the structure of the Laves phase of C14 type. The subsequent replacement of iron atoms by aluminum atoms leads to the formation of a two-phase region ($0.5 < x < 0.8$) in the system consisting of phases with hexagonal (C14) and cubic (C15) structures. Finally, in the region $0.8 \le x \le 1$ the cubic C15 structure. It can be seen that the parameters of the unit cells grow linearly with an increase in the concentration of aluminum in both the C15 and the C14 structures. In this case the relative change in the volume of the unit cell with the complete replacement of Fe atoms by atoms is Al in the $Yb(Fe_{1-x}Al_x)_2$ system 28.8%.

The structural phase transitions depending on the concentration of aluminum are also observed in the case of the systems $Pr(Fe_{1-x}Al_x)_2$ and $Yb(Fe_{1-x}Al_x)_2$. The only difference is that in the region of high aluminum concentrations, the width of two-phase region decreases and the region of the first structural transition shifts to the right to large values of x (in the first system, to the value x = 0.2, and in the second x = 0.4).

Important information about magnetism of these compounds can be given by the simultaneous study of their magnetic properties and hyperfine interactions. The Curie temperatures of $Pr(Fe_{1-x}Al_x)_2$ alloys were determined obtained from direct magnetic measurements carried out in the field up to 10 kOe, and Mossbauer studies depending on the aluminum concentration (Fig. 2). It can be seen that in the entire magnetic ordering region the Curie temperature data completely coincide within the limits of measurement errors. At x > 0.4 this system is paramagnetic in the region of room temperatures the same as the system of $Yb(Fe_{1-x}Al_x)_2$ alloys for $x \ge 0.3$ [7]. Consequently, aluminum concentrations x = 0.4 and x = 0.3 are points of the order-disorder magnetic phase transition for the systems of $Pr(Fe_{1-x}Al_x)_2$ and $Yb(Fe_{1-x}Al_x)_2$ alloys, respectively.

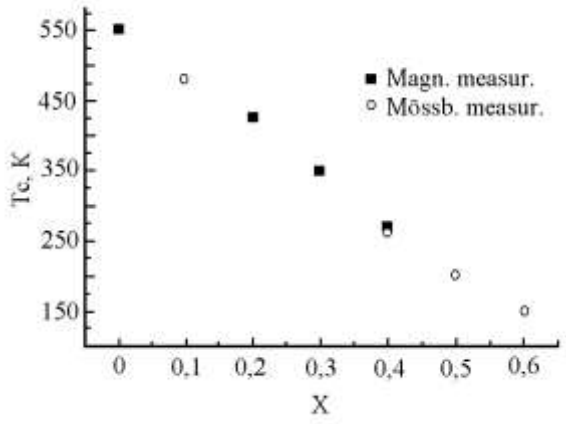

Fig. 2. Curie temperature dependence of alloys of $Pr(Fe_{1-x}Al_x)_2$ system on aluminum concentration

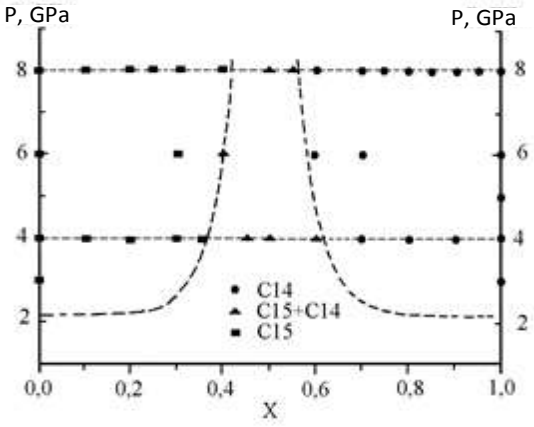

Fig. 3. Phase diagram of system $Yb(Fe_{1-x}Mn_x)_2$.

B. *Structure and magnetic properties of alloy systems $R(Fe_{1-x}Mn_x)_2$, where R = Yb, Ho, Tb, Dy*

The issue of the nature of magnetism of manganese subsystem in RMn_2 compounds generates a lot of interest. It is believed that the magnetic ordering of manganese subsystem in the GdMn2 and TbMn2 compounds has metamagnetic properties, while in another RMn_2 compounds the manganese sublattice is not ordered. Therefore, it was interesting to study the effect of manganese subsystem on the magnetism of alloys $R(Fe_{1-x}Mn_x)_2$.

The alloys of the $Yb(Fe_{1-x}Mn_x)_2$ system of the following compositions were prepared along x: 0, 0.1, 0.2, 0.3, 0.35, 0.4, 0.45, 0.5, 0.55, 0.6, 0.65, 0.7, 0.75, 0.8, 0.85, 0.9, 0.95, 1.0. The $Ho(Fe_{1-x}Mn_x)_2$ system was prepared the same as was the $Dy(Fe_{1-x}Mn_x)_2$ system, mainly with a step of 0.1 in the region of single-phase samples and with a smaller step of 0.05 in the region of phase transformations. The $Tb(Fe_{1-x}Mn_x)_2$ system was prepared with a step of 0.2 and with a smaller step of 0.1 in the region of structural phase

It is known that the intermetallic compound $YbFe_2$ is isotype to the cubic C15 Laves phase, and the intermetallic compound $YbMn_2$ is the hexagonal C14 Laves phase. It was found that with an increase in manganese concentration in the $Yb(Fe_{1-x}Mn_x)_2$ system alloys, the C15 structural type is replaced by C14 with the formation of C14+C15 two-phase region, and the length of the phase fields in the phase diagram of this system are determined by the concentration of manganese x and pressure P (Fig. 3).

Near the manganese concentration x = 0.5, the phase diagram of the $Yb(Fe_{1-x}Mn_x)_2$ system is characterized by the presence of two-phase region, and the width of this region decreases with the increasing pressure at which the synthesis was performed. The analysis of changes in the phase composition of alloys showed that packing defects appear inside the two-phase region.

The alloys of quasi-binary system of $Ho(Fe_{1-x}Mn_x)_2$ under normal synthesis conditions crystallize either in the C15 structural type ($0 \le x \le 0.65$) or in the C14 structural type ($0.75 \le x \le 0.1$) of the Laves phases depending on the manganese concentration. In a narrow concentration range of $0.65 < x < 0.75$, a two-phase structure C14+C15 is formed in the system. We have carried out the synthesis of the $Ho(Fe_{1-x}Mn_x)_2$ system at pressures up to 8.0 GPa. The X-ray examination of the samples showed that synthesis at high pressures does not lead to any change in phase boundaries of C14 and C15 phases and to noticeable changes in their crystal structure characteristics.

A more complex type of structural phase diagrams is demonstrated by the alloys of the systems $Dy(Fe_{1-x}Mn_x)_2$ and $Tb(Fe_{1-x}Mn_x)_2$. In both systems, at synthesis pressures below 2 GPa in the whole concentration range $0 \le x \le 1$, the alloys are single-phase and isotype to the cubic C15 Laves phase. With an increase in pressure at which the synthesis was performed, in the region rich in manganese ($0.8 \le x \le 1.0$), a hexagonal phase is formed in the system, isotype to the C14 Laves phase and separated from the C15 phase of the C15 phase by the two-phase C14+C15 region. Thus, in the regions with high concentrations of manganese the alloys can exist in two polymorphic modifications: at high pressures - in the hexagonal phase of C14 and at low pressures - in the cubic C15 phase.

The set of experimental data on the study of the temperature dependence of magnetization of the $Yb(Fe_{1-x}Mn_x)_2$ system alloys and the Mossbourg effect indicates that complex magnetic interactions occur in the 3d sublattice, which lead to the formation of a pseudobinary $Yb(Fe_{1-x}Mn_x)_2$ system of magnetic structure not of ferrimagnetic but of a more complex type [8].

Magnetostriction is regarded as a sensitive parameter to a change in the type of magnetic interactions [9]. It is known that magnetostriction is a change in the size of a magnet when its magnetic state changes. There is a distinction between longitudinal and transverse magnetostriction. We have studied the magnetostriction properties of alloys of the $Ho(Fe_{1-x}Mn_x)_2$ system in a wide temperature range from nitrogen temperatures to 400 K in the field up to 11 kOe. The longitudinal magnetostriction of alloys is negative in the region of nitrogen

temperatures; however, in the region of room temperatures it changes. The transverse magnetostriction behaves similarly. It changes from positive to negative sign. Summing up the obtained data on the inversion of constants signs of longitudinal and transverse magnetostriction depending on the temperature and the magnetic field, we can represent them in the form of a field – temperature diagram (Fig. 4).

The figure shows that the magnetic phase diagram of $HoFe_2$ compound consists of two regions one of which I corresponds to $\lambda \parallel < 0$, $\lambda > 0$. This region exists at low fields for practically the entire temperature range from 95 K to T_C. As the magnetic field increases, this region narrows in temperature, and the region II with $\lambda \parallel > 0$ and $\lambda < 0$ expands, as in the case of alloy x = 0.2. In the alloy of composition x = 0.6, at temperatures above the nitrogen, the entire field of phase diagram occupies the region of type II. This effect was encountered earlier both in pure rare-earth metals and in alloys, for example, in Tb – Y and Dy – Y. It is considered a magnetic phase transition from ferromagnetic to helicoidal state [10], i.e. we observe a magnetic order-to-order phase transition along the phase separation line.

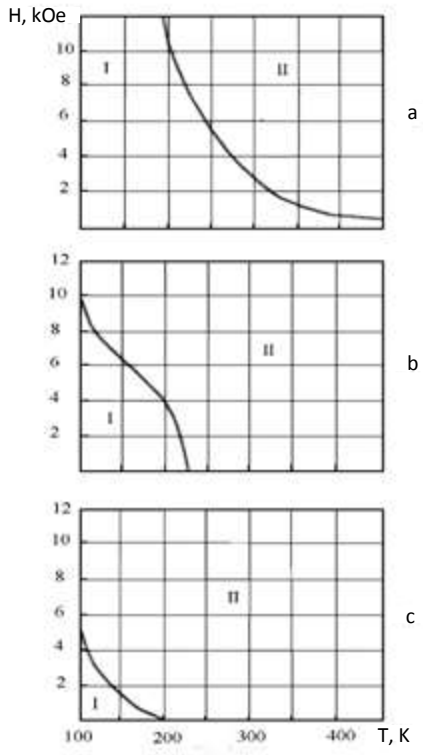

Fig. 4. Phase diagrams of alloys of $Ho(Fe_{1-x}Mn_x)_2$ system in the field – temperature coordinates for compositions c x = 0(a), 0.2 (b), 0.4 (c).

C. Structure and magnetic properties of quasi-binary alloys $Nd(Fe_{1-x}M_x)_2$ (where M = Mn, Co and Ni)

The samples of alloys of the $Nd(Fe_{1-x}Co_x)_2$ system had compositions along x: 0, 0.2, 0.4, 0.6, 0.8, 1.0. In the $Nd(Fe_1$-$xNix)_2$ system there were the following compositions along x: 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1 and $Nd(Fe_{1-x}Mn_x)_2$ – x = 0, 0.1, 0.2, 0.3, 0.4, 0.5. The unit cell parameters of the compounds $Nd(Fe_{1-x}Co_x)_2$ and $Nd(Fe_{1-x}Ni_x)_2$ and the volume per equation unit monotonously decrease with the increasing concentrations of Co and Ni, whereas the volume $V_{\phi.e.}$ increases monotonously in the $Nd(Fe_{1-x}Mn_x)_2$ system. The unit cell parameters of the $NdFe_2$ source for all intermetallic systems are as follows: a = 7.447±0.003 Å, V_{cell} = 412.99±0.08 Å^3, $V_{f.e.}$ = 51.62±0.06 Å^3 (Fig.5).

It should be noted that non-linearity is clearly visible on the $V_{\phi.e.}$ (x) concentration dependence curve. The deviation from Vegard rule says that the simple model of dense packings of atoms of different sizes in this system does not work. It can be seen that the replacement of Fe atoms by an impurity metal in the $Nd(Fe_1$-$xMnx)_2$ system is accompanied by an increase in the volume of the unit cell by almost 6%.

Whereas in the compounds of $Nd(Fe_{1-x}Co_x)_2$ and $Nd(Fe_{1-x}Ni_x)_2$ systems 5% monotonic decrease in the unit cell volume occurs when the concentration x varies from 0 to 1.

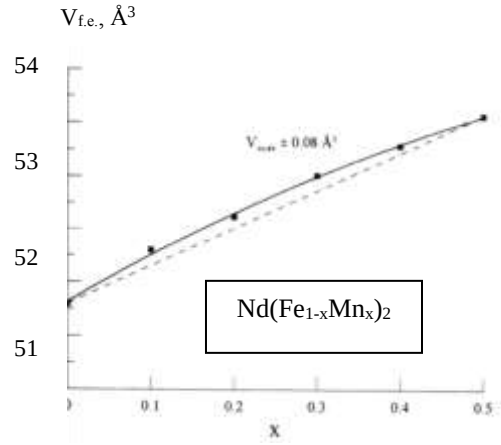

Fig. 5. Concentration dependence of volume attributable to the formula unit $V_{\phi.e.}$ for the system $Nd(Fe_{1-x}Mn_x)_2$.

IV. CONCLUSION

Synthesis at high pressures is one of the conditions for obtaining HMI compounds of rare-earth metals Yb, Pr and Nd with 3d transition metals. Studies have shown that it is possible to obtain solid solutions in the entire region of iron substitution in 3d sublattice by nonmagnetic aluminum.

An exception is the $Y(Fe_{1-x}Al_x)_2$ system as it was possible to synthesize alloys which are homogeneous solid solutions of aluminum atoms in 3d sublattice only in the concentration range of $0 \le x \le 0.2$. The methods of temperature magnetic and Mossbauer measurements in these alloys detected magnetic phase transitions of the "order-disorder" type. At an aluminum concentration of x = 0.15 the system changes from a ferromagnetic condition to paramagnetic one at room temperature.

In the compounds of the $Yb(Fe_{1-x}Al_x)_2$ system, two structural phase transitions are observed. In the region of aluminum concentrations $0<x<0.45$ and $0.8<x<1.0$ these alloys have the cubic structure of the Laves C15 phase. The region of

alloys of intermediate compositions $0.55 \leq x \leq 0.70$ has the structure of the hexagonal C14 Laves phase. Both structures are separated from each other by the concentration regions consisting of two phases.

For the $Pr(Fe_{1-x}Al_x)_2$ system, in addition to structural phase transitions, the magnetic order-disorder phase transitions were also detected. It is shown that the Curie temperature of the alloys of the system decreases linearly depending on the nonmagnetic component. In this case, the data of direct magnetic measurements exactly coincide with the Curie temperature determined from the temperature studies of the Mossbauer effect.

As for the Nd(Fe1-xAlx)2 system, besides the single-phase regions, the order-disorder phase transition temperatures are also determined and it is shown that the Curie temperatures in this system decrease linearly depending on the amount of nonmagnetic component. At x = 0.3, a magnetic phase transition (concentration) from the ferromagnetic to the paramagnetic state is observed.

In high-pressure phases, structural phase C15→C14 transitions are observed where the substitution in 3d sublattice is manganese atoms $Yb(Fe_{1-x}Mn_x)_2$, $Ho(Fe_{1-x}Mn_x)_2$, $Tb(Fe_{1-x}Mn_x)_2$, $Dy(Fe_{1-x}Mn_x)_2$. In the phase diagram the phases are separated from each other in the composition-pressure coordinates by two-phase region consisting of a mixture of phases C14+C15 and packaging defects of deformation and twin type.

For the $Ho(Fe_{1-x}Mn_x)_2$ system a magnetic field-temperature phase diagrams were constructed basing on the studies of magnetoelastic properties. The transitions observed are considered as magnetic phase transitions from ferromagnetic to helicoidal state.

We managed to obtain alloys based on neodymium $Nd(Fe_{1-x}Co_x)_2$, $Nd(Fe_{1-x}Ni_x)_2$ и $Nd(Fe_{1-x}Mn_x)_2$ isotype to C15 structure, in the concentration range $x = 0 \div 1$ for the first two systems and $x = 0 \div 0.5$ for the last one.

According to our data, the unit cell parameters of the compounds $Nd(Fe_{1-x}Co_x)_2$ and $Nd(Fe_{1-x}Ni_x)_2$ and the volume per formula unit monotonously decrease as the concentrations of nickel and cobalt in the 3d sublattices increases. In the $Nd(Fe_{1-x}Mn_x)_2$ system with an increase in the concentration of manganese atoms the volume per formula unit monotonously increases.

Thus, in the high pressure phases, the results of which are presented in this work, several types of phase transformations are observed: structural phase transitions, magnetic phase transitions of the order-order type, and magnetic phase transitions of the order-disorder type.

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