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ABSTRACT

The pressure-temperature magnetic phase diagram was determined for Fe-Rh alloys, ferromagnetic down to 4.2K, from room temperature to the Curie point (750 K) and for pressure up to 100 kbar. A pressure-induced first order ferromagnetic-antiferromagnetic phase transition line was found with an inhomogeneous, mixed phase existing at pressures lower than 50 kbar. A new, qualitative model is proposed to explain the phase transitions, the absence of magnetic moment on Rh atoms in the AF state and the shape of the p-T diagram. The model is based on the excitonic antiferromagnetism of semimetallic Fe-Rh and it is connected with the peculiarities of the electronic structure and the shape of the Fermi surface.

АННОТАЦИЯ

В настоящей работе представлены результаты экспериментального исследования влияния высокого давления на магнитные свойства ферромагнитного сплава $\text{Fe}_{51.5}\text{Rh}_{48.5}$. При повышении давления путем фазового перехода первого рода сплав переходит в антиферромагнитное состояние. Предложена качественная модель, объясняющая последовательность магнитных переходов в сплаве FeRh, связана с экситонным антиферромагнетизмом и особенностями электронной структуры и формы поверхности Ферми.

KIVONAT

Atmoszférikus nyomáson ferromágneses Fe-Rh ötvözetek mágneses p-T fázisábráját határoztuk meg 300-750 K hőmérséklettartományban 100 kbar nyomásig. Nyomás hatására elsőrendű ferromágneses-antiferromágneses fázisátalakulás játszódik le az ötvözetben. Új modellt javasolunk a fázisátalakulás mechanizmusának, a p-T fázisábrának és a Rh momentum kérdésének leírására. A modell alapja a FeRh exciton antiferromágneses állapota és a Fermi felület alakjának sajátosságai.

INTRODUCTION

In the equi-atomic ordered $\text{Fe}_{50}\text{Rh}_{50}$ alloy a first-order magnetic phase transformation takes place at about 320 K, when the alloy transforms to a ferromagnetic (FM) phase from a low temperature antiferromagnetic structure (AF). The transformation is isomorphous, the crystal structure does not change, but the volume of the elementary cell increases by 0.92 % [1]. Under the influence of pressure the first-order transition temperature increases, stabilizing the AF phase; the second-order Curie point of ferromagnetic - paramagnetic (FM-PM) transition decreases [2].

All the physical properties of the Fe-Rh alloys are strongly dependent on the composition, on increasing the iron content by 1-2 % the alloy becomes ferromagnetic even at low temperatures [3]. The lattice parameter - as in the case of the AF-FM transition - increases. According to Shirane [4] for $\text{Fe}_{50}\text{Rh}_{50}$, $a = 2.986 \text{ \AA}$; $\text{Fe}_{51}\text{Rh}_{49}$, $a = 2.993 \text{ \AA}$; $\text{Fe}_{52}\text{Rh}_{48}$, $a = 2.989 \text{ \AA}$.

The crystal structure of FeRh in the paramagnetic state is simple cubic with two atoms in the elementary cell (CsCl-type, O_h^1 group). In the AF state, according to the different orientations of their magnetic moments, the iron

atoms form two fcc magnetic sublattices, the rhodium atoms are ordered in a simple lattice with two times smaller periodicity. The elementary cell doubles and contains 2 Fe and 2 Rh atoms. The space group changes to O_h^5 .

Electronic specific heat measurements of AF and FM samples of FeRh revealed [5] that in the FM phase this quantity is 3-4 times higher than in the AF state. Shinkel et al. suggested that FeRh has the character of a semimetal [6]. On the basis of the above data one can suppose that the basic mechanism responsible for the AF-FM transition taking place under thermal or compositional changes is the peculiarities in the density of states at the Fermi level and the shape of the Fermi surface of the alloys itself. One may assume that the changes in the band structure required for the transition to the AF state could be generated by hydrostatic pressures through volume decrease.

EXPERIMENTAL

The electrical resistivity of ferromagnetic Fe-Rh alloys was measured on changing the temperature or the pressure acting on the alloy. Magnetization measurements performed on a vibrating sample magnetometer showed that the alloys are ferromagnetic even at $T = 4.2$ K, the saturation magnetiza-

tion for $\text{Fe}_{51.5}\text{Rh}_{48.5}$ at 4.2 K is 137.3 emu/g, practically equal to the value for the equiatomic alloy (Fig.1) . The Curie temperature $T_C = 750$ K; for the stoichiometric alloy $T_C = 665$ K.

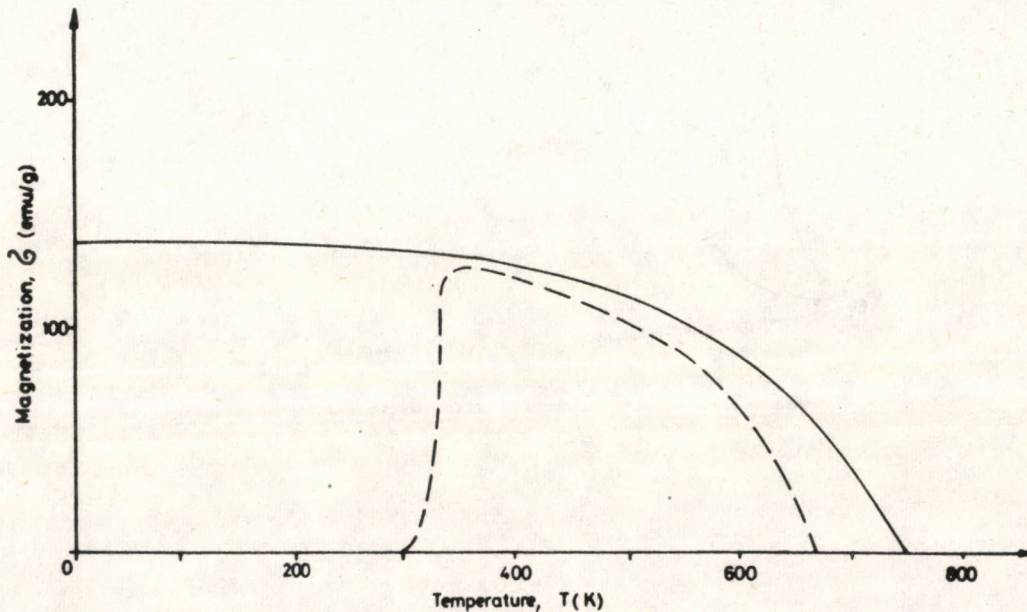


Fig.1. Temperature dependence of the saturation magnetization of $\text{Fe}_{51.5}\text{Rh}_{48.5}$ alloy compared with the magnetization of $\text{Fe}_{50}\text{Rh}_{50}$ /dashed line/ showing the AF-FM transition

The pressure up to 100 kbar was generated in a "toroid" type apparatus in a cell filled with polysiloxane fluid. The electrical resistivity was measured by the four-point method.

Figure 2 reproduces the pressure dependences of the resistivity of three Fe-Rh alloys measured at room temperature. One of them is antiferromagnetic ($\text{Fe}_{50}\text{Rh}_{50}$), the two others are ferromagnetic (51.5 and 52.0 at% Fe). The pressure effect is different for the antiferromagnetic and ferromagnetic alloys: the pressure dependence of the AF resistivity is very small, resembling pure metals, whereas the resistivity of the

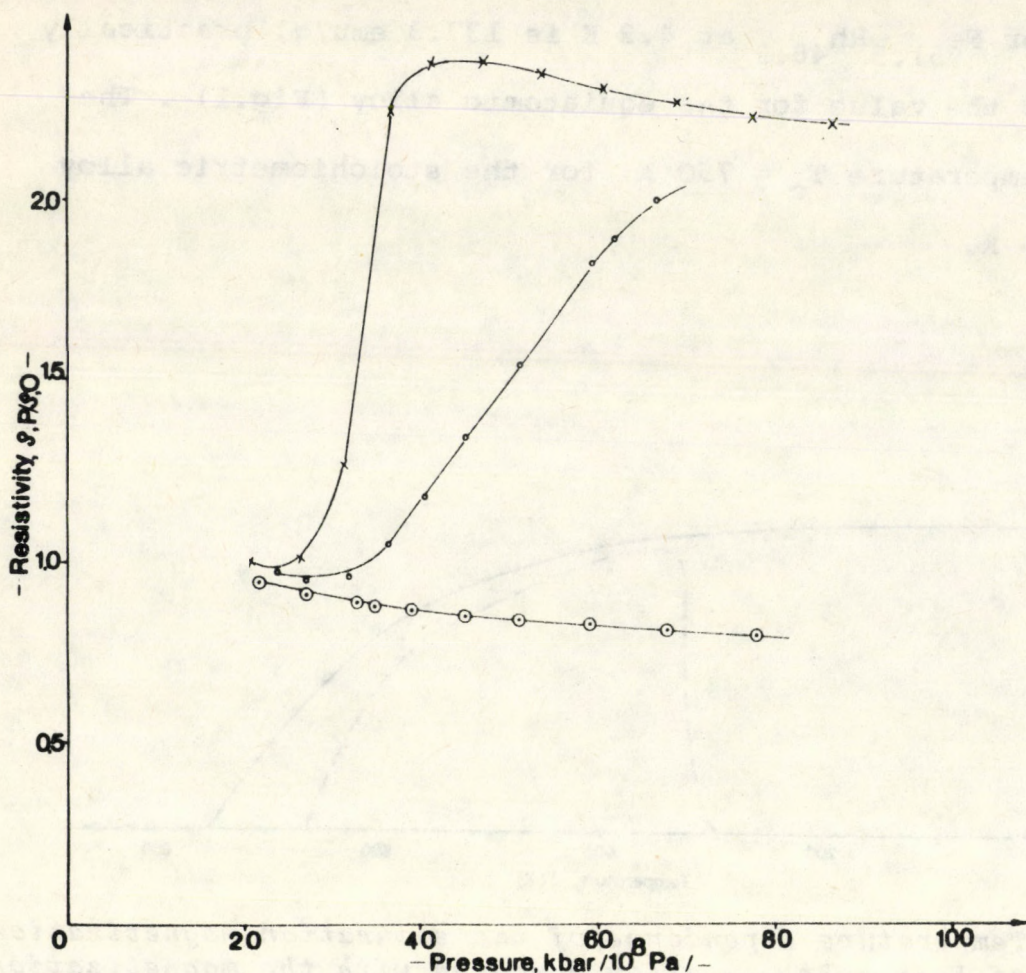


Fig. 2. Pressure dependence of the electrical resistivity of Fe-Rh alloys measured at room temperature. ($\rho(o)$ -resistivity at atmospheric pressure, $\rho(p)$ at pressure p), \times - $Fe_{51.5}Rh_{48.5}$; o - $Fe_{52}Rh_{48}$; \bullet - $Fe_{50}Rh_{50}$.

FM alloys increases rapidly with pressure. For $Fe_{51.5}Rh_{48.5}$ at $p = 25$ kbar the pressure dependence of the resistivity is very similar to the case of the equi-atomic FeRh, when the first-order FM-AF magnetic phase transition takes place at room temperature on increasing the pressure [2].

For the sample with 52 % Rh the resistivity increase is more smooth and extends over a pressure region of 50 kbar. We assume that in this case an inhomogeneous magnetic structure is formed.

The isobaric temperature dependence of the electrical resistivity of the $\text{Fe}_{51.5}\text{Rh}_{48.5}$ alloy was investigated in detail, as is illustrated in Fig.3. The resistivity - temperature curves reveal a jump in the resistivity on decreasing the temperature, according to an FM-AF transition. On increasing the pressure, the height of the jump and the volume of the AF phase increase, showing that there exists a given temperature - pressure range for the co-existence of the FM and AF phases. The anomalously large thermal hysteresis of the transition supports the idea of the inhomogeneous magnetic structure.

On further increasing the pressure the height of the jump does not change in a given pressure interval (50-70 kbar); above this it starts to decrease. On increasing the pressure the thermal hysteresis of the transition decreases too.

The anomalous behaviour of the resistivity is related to the magnetic phase changes of the ferromagnetic $\text{Fe}_{51.5}\text{Rh}_{48.5}$ alloy occurring under high pressures (Fig.4). At pressures under 50 kbar and temperatures below the Curie point there exists a broad region of ferromagnetic spin ordering which, on decreasing the temperature, via first-order phase transition

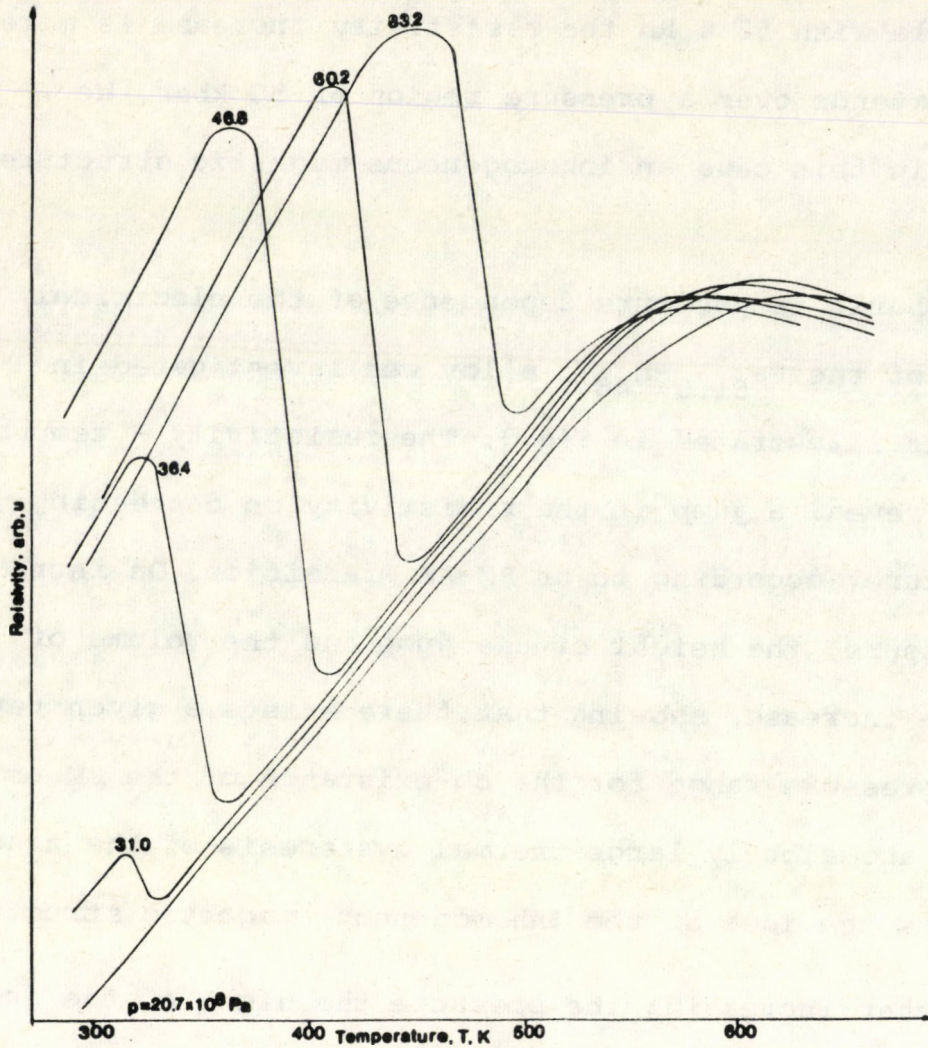


Fig.3. Isobaric temperature dependences of the electrical resistivity of $Fe_{51.5}Rh_{48.5}$ measured at different pressures

transforms to an inhomogeneous magnetic structure containing ferro- and antiferromagnetic components simultaneously. At higher pressures ($p > 50$ kbar), a situation familiar from the stoichiometric FeRh alloy can be seen: under T_c (second-order PM-FM transition) on further decreasing the temperature via

first-order transition a homogeneous AF state forms, with substantially narrower hysteresis. At higher pressures the alloy behaves as the stoichiometric one, the interval of the existence of the FM state becomes narrower, the resistivity jump decreases and the AF phase tends to "absorb" the FM phase. Unfortunately, pressures up to 100 kbar are not enough to remove the FM phase completely, i.e. to reach the triple-point of co-existence of the FM-PM-AF phases. According to our extrapolation this will happen at about 130 kbar.

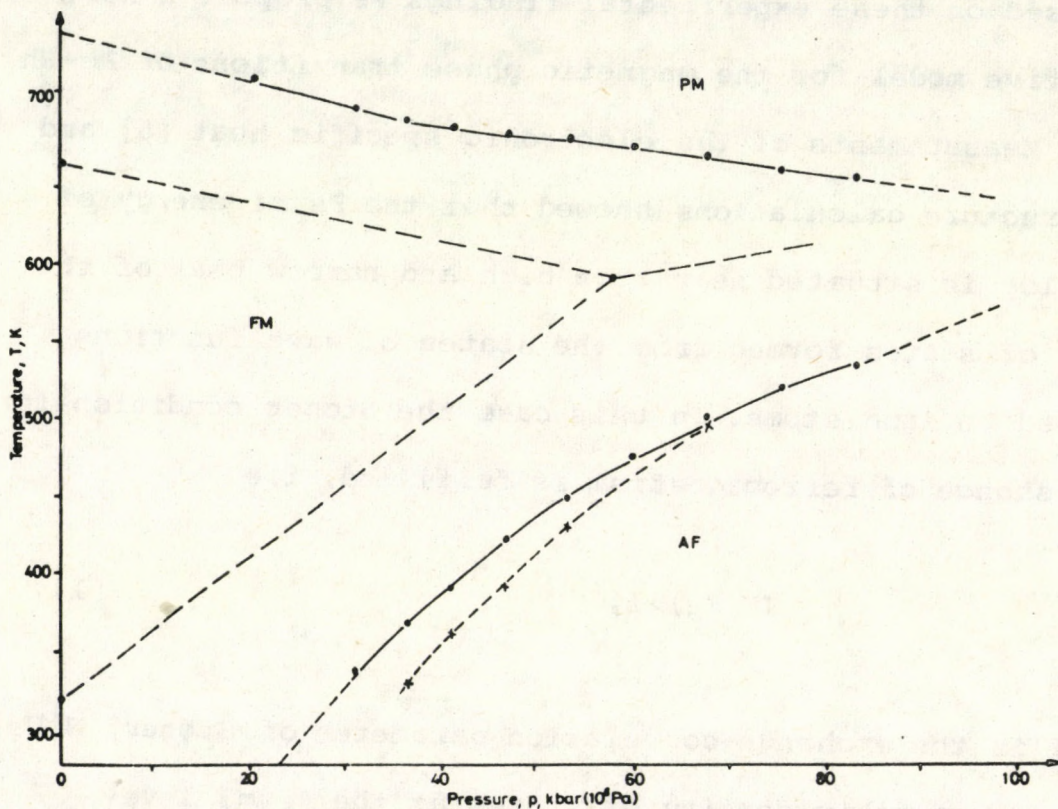


Fig.4. p - T magnetic phase diagram of the $Fe_{51.5}Rh_{48.5}$ alloy compared with the phase diagram of equi-atomic $FeRh$ [2]

DISCUSSION

The magnetic p-T phase diagram of the $\text{Fe}_{51.5}\text{Rh}_{48.5}$ alloy shows (Fig.4) that at $p \approx 0$ and $T \approx 0$ it is ferromagnetic, at higher pressures the antiferromagnetic state is stable at low temperatures. For $T < 370$ K and $p > 50$ kbar the situation is similar to the case of the equiatomic FeRh, and above the triple point the magnetic order - when it exists - is antiferromagnetic at any temperature.

Based on these experimental findings we propose a new, qualitative model for the magnetic phase transitions of Fe-Rh alloys. Measurements of the electronic specific heat [5] and band structure calculations showed that the Fermi energy of this alloy is situated near to a high and narrow peak of the density of states formed from the states of wave functions localized on iron atoms. In this case the Stoner condition for the existence of ferromagnetism is fulfilled, i.e.

$$IN(E_F) > 1, \quad (1)$$

where I is the exchange-correlation parameter of Stoner, $N(E_F)$ is the paramagnetic density of states at the Fermi level. Consequently, the ferromagnetic state is energetically favourable. Under pressure the bands are broadened, $N(E_F)$ decreases, inequality (1) weakens and the free energy δE_{FM} of the FM state increases in accordance with

$$\delta E_{FM} = k[1 - \ln(E_F)] , \quad (2)$$

where $k = m_0/N(E_F)$ and m_0 is the spontaneous magnetic moment. Consequently, the region of the existence of the FM phase is narrowed from above.

At the same time, there must be a reason for the low temperature AF phase to be favoured when compared with ferromagnetism. The drastic decrease of the density of states in the AF phase shows that on the Fermi surface of the Fe-Rh alloys (similarly to the Cr) there are such electron and hole parts which could be matched together on translation by a given \underline{Q} vector (nesting). At the same time, this \underline{Q} is the wavefunction of the spin density wave, leading to the changes in the symmetry of the crystalline potential:

$$\epsilon_1(\underline{k}) = -\epsilon_2(\underline{k} + \underline{Q}) \quad (3)$$

for all \underline{k} . It is worth mentioning that the high density of states in the PM phase leads to a situation where the effective constant of triplet pairing for the electrons of the first and second bands will be large enough, i.e. a possibility occurs for AF ordering that is much more favourable than in the case of Cr, for which $N(E_F)$ is relatively low.

If the symmetry of the untransformed (PM) and transformed (AF) phases is known, then \underline{Q} can be determined. For our case, the symmetry in the PM phase is O_h^1 , in the AF phase it is O_h^5 with the elementary cell doubled. It can easily be shown that

for this case $Q = 2\pi/a(1,1,1)$. A new plane in the Brillouin zone (BZ) crosses the centre of this vector and all the states outside this new plane have to be translated inside the new fcc BZ. The Q vector is simply equal to the vector joining the Γ and R points of the simple cubic BZ. We have to find such nesting pockets on the Fermi surface which are centred at the Γ and R points, respectively. In the work of Khan [7], unfortunately, there are no data concerning the shape of the Fermi surface, and the band structure is given only in high symmetry directions. However, from his calculations it unambiguously follows (Fig. 2 of [7]) that near to the Γ points a large volume electron pocket is centred and along the Γ -R line (about half way along the line) this electron pocket is in contact with a hole pocket centred at R points. Due to the same symmetry of the Γ and R points (from the viewpoint of their irreducible representations), it is reasonable to assume that the shape of the electron and hole pockets is similar and the condition for nesting (3) will be fulfilled.

The model gives an explanation for the absence of the magnetic moment of the Rh atoms in the AF state. Indeed, the spin density wave with a wave vector of Q

$$P(r) = m_0 \cos(Qr) \quad (4)$$

corresponding to nesting at the Γ and R points, will have zeros at points of $a(1/4, 1/4, 1/4)$ and $a(3/4, 3/4, 3/4)$, where

the Rh atoms are located.

At low temperatures the Fe-Rh alloys are unstable against transition to FM or AF states because the difference between the free energies of the two states is very small. But the different temperature dependences of the free energies of the FM and/or AF states may lead to the replacement of the low temperature AF phase by a new FM state before the AF phase loses its absolute stability. In view of this, the real Néel temperature will never be reached and in the ferromagnetic Fe-Rh alloys such as $\text{Fe}_{51.5}\text{Rh}_{48.5}$ the AF phase exists in a "latent" state.

It is easy now, to understand why the AF phase disappears under small deviations from stoichiometry [3]. Compositional differences spoil the fulfillment of the nesting conditions (3), and suppress the exciton-antiferromagnetic state. The gain in free energy at the formation of the excitonic antiferromagnetic state according to [8] is

$$\delta E_{\text{AF}} = -N_{\text{A}}(E_{\text{F}}) \{ \Delta^2 + 2\mu_{\text{O}}^2 - \beta(\mu^2 - \mu_{\text{O}}^2) \} \quad \text{at } T=0, \quad (5)$$

where Δ is the AF gap in the band structure, $N_{\text{A}}(E_{\text{F}})$ is the density of states in the nesting bands, μ_{O} and μ are the nesting imperfections or the chemical potentials of the initial and transformed phases respectively compared with the Fermi energy of the ideal crystal, $\beta = N(E_{\text{F}})/2N_{\text{A}}(E_{\text{F}})$ is the power

of the electronic reservoir, which is less than 1/2 according to specific heat measurements. For ideal nesting the free energy of the AF phase is

$$\delta E_{AF} = -N_A(E_F) \{ \Delta_0^2 - 2\mu_0^2 \} \quad (6)$$

where Δ_0 is the gap for ideal nesting. It can be seen that when deviations from stoichiometry increase, the gain in energy of the AF phase compared with the FM phase decreases.

From the exciton theory [9] follows the second order character of the PM-AF phase transition, too; this was experimentally demonstrated by us earlier [2].

The effect of the pressure on the energy balance of the AF and FM phases is somewhat opposed to the effect of nonstoichiometry: hydrostatic pressure practically does not change μ_0 , that is, the measure of the fulfillment of nesting conditions, but the broadening of the bands according to (1) and (6) decreases the free energy of the FM state more than that of the AF phase because $N_A(E_F) \simeq 2/3 N(E_F)$. Therefore the line of the first-order AF-FM phase transition will be an increasing function of the pressure, as was demonstrated in our earlier publications (see ref. [2]). Such an unusual pressure dependence of the Néel point is connected with the fact that the real Néel point is located at a much higher temperature than the AF-FM transition temperature and the magnetic phase diagram of the Fe-Rh

alloys is determined by the competition of two possible magnetic structures, both of which are connected with the peculiarities of the band structure of the material.

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