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## Possible Types of Ordering Cation Vacancies in Structures of the NiAs Type

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*A connection was found between the type of vacancy distribution and the magnetic properties of non-stoichiometric ferrimagnets such as pyrrhotite. Within the framework of the molecular-field approximation, a theoretical explanation was given to the dependence of the magnetization on the temperature of magnetically ordered compounds containing cation vacancies in the crystal structure. On the basis of the proposed model of the vacancy behavior, the theoretically possible dependences of the magnetization on the temperature were presented.*

*Keywords: pyrrhotite, pyrite, crystal structure, cation vacancies, phase composition, ferrimagnet.*

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## Introduction

The topicality of the research on minerals obtained under laboratory conditions at high temperatures and their subsequent exposure for a long time (about several decades) is of interest nowadays, since it allows to model environmental processes in the earth's crust. One of the minerals that can be obtained under laboratory conditions is pyrrhotite. The crystal structure (such as NiAs with cation vacancies) and the physical properties of this mineral are well studied both in environmental and in synthetic samples, but some points remain unclear.

The pyrrhotites formed immediately after synthesis and pyrrhotites under the same conditions after decades can differ significantly both in physical properties and in crystal structure. This is explained by the fact that in the first case the samples are in a metastable phase state, and

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in the second case in a stable phase state. In one and the same rock we may find pyrrhotites with different chemical compositions. The physical mechanisms that lead to such changes are unclear. The decay of one phase into two or three (the ratio of Fe/S in the rock in this case is the same) undoubtedly causes interest among geologists. In real-life it is necessary to conduct observations for a long time under certain conditions, which is difficult to implement in practice. In addition, the specific magnetic properties of pyrrhotites, which are reflected in the change in magnetization according to the temperature are also of interest, no corresponding to the Curie or Neel temperature in the cycles of heating, cooling, etc.

The purpose of the research was to study the phase composition, the crystal structure, and the magnetic properties of iron sulfides both in the metastable state and their transition to a stable phase state at room temperature.

## 1. Samples and methods of their research

The objects of the research were pyrrhotites obtained as a result of high-temperature decomposition of environmental monocrystal pyrite in low vacuum conditions ( $10^{-2}$  Pa). Samples were made by calcinating pyrite in quartz ampoules. Calcination of pyrite was carried out at the temperature from 400 to 1200°C for 1 hour. Two series of samples were studied. Samples of the A series after annealing were quenched in running water, and the samples of the B series were slowly cooled at a rate of 20 min to 20°C.

The crystal structure of the samples was studied by X-ray fluorescence analysis and X-ray photoelectron spectroscopy using Co ( $K_{\alpha}$ ) radiation, as well as various thermomagnetic methods. The speed of the diffraction patterns was 1 min in continuous mode and 0.001 sec in discrete mode. The diffraction pattern was taken using a  $\beta$ -radiation filter from iron. Thermomagnetic measurements were carried out on a ballistic installation in a field of 1 kOe at the temperature from 20 to 360°C.

## 2. Experimental results

A large number of sulfides, selenides and tellurides in transitional metals form a dense hexagonal packing. In the composition corresponding to formula BX, where B and X are the metal and nonmetal atoms, with a B8 structure (of the NiAs type), the metal atoms have octahedral coordination in the lattice of sulfur atoms. If we consider the structure in the direction perpendicular to the "c" axis, it can be represented with a sequence of layers: atoms of one kind – X – B – X – B.

Chalcogenides are of some interest from the point of view of studying vacancies. The number of vacancies in their structure is determined by the composition, namely the formula unit. For example, the formula for pyrrhotite is represented as  $Fe_{1-n}S$ , where n is the number of vacancies, that is, the average number of vacancies per one iron atom (the density of vacancies). In addition, chalcogenides can be used to study the ordering of vacancies in a structure with a long-range magnetic order. Magnetic properties in nonstoichiometric ferrimagnets are closely related to the distribution of cation vacancies in the structure [1, 2]. For example, in the structure of pyrrhotite, a ferromagnetic spin ordering is realized in the basal planes and an antiferromagnetic order is realized in the neighboring planes.

Studying pyrrhotites obtained as a result of the pyrite-pyrrhotite transition [3, 4] reveals the dependence of the magnetic properties and the crystal structure on the temperature and on the

time and temperature of their annealing.

Fig. 1 shows the dependence of the magnetization and the interplanar distance of the obtained samples on the pyrite annealing temperature. Curve 1 corresponds to samples of the A series; curve 2 of the B series. Curves 3 and 4 show the changes in the interplanar distances  $d_{102}$  for the ferrimagnetic and antiferromagnetic ordering of the sublattices.

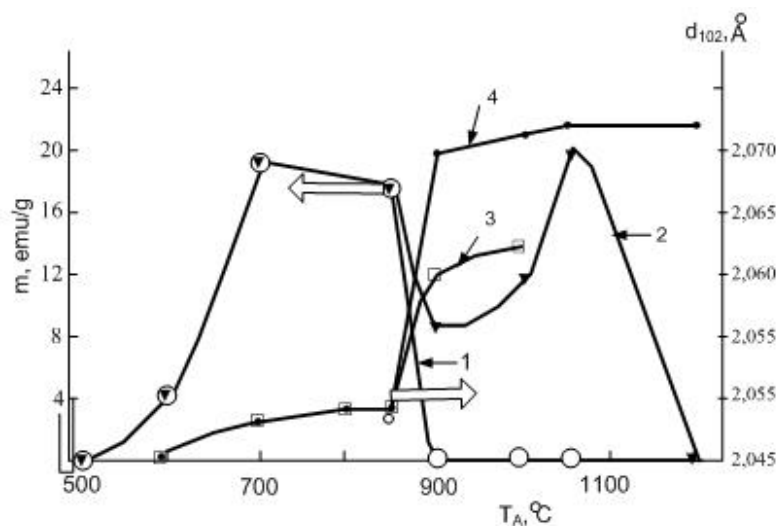


Fig. 1. The dependence of the magnetization (curves 1, 2) and the interplanar distance  $d_{102}$  (3, 4) of pyrrhotites on the annealing temperature and cooling conditions

In the interval of the TA annealing temperatures from 500 to 1000 °C, the two-phase samples were obtained, consisting of pyrite and pyrrhotite. The percentage of these phases depends on TA. The rise in magnetization is explained by a decrease in the percentage content of the pyrite paramagnetic phase and a simultaneous increase in the pyrrhotite ferrimagnetic phase. In the annealing temperature range of 650–850 °C, all the obtained samples had a high magnetization. At the TA temperatures from 900 to 1050 °C, samples of the A series became antiferromagnetic, and samples of the B series became ferrimagnetic. The decrease and then the increase of the magnetization for the samples of the B series on curve 2 is explained by the phase transition of the hexagonal pyrrhotite to the monoclinic ( $\beta_5 - \beta_6$  according to the labeling on the phase diagram [5, 6]), at which partial vacancy disordering takes place. A similar effect is described in [7].

Fig. 2 shows the dependence of magnetization on the temperature for the samples after annealing at different temperatures. Ferrimagnetic pyrrhotites with a high magnetization value (annealing temperature was 700 and 850 °C) have the usual curve  $m(T)$  (Fig. 2a and 2b).

As we have already noted, the B-series samples obtained as a result of the pyrite calcination at the temperatures from 900 to 1000 °C are pyrrhotites of intermediate type with partial vacancy ordering. The curve  $m(T)$  in Fig. 3C corresponds to a sample of the B series, which was annealed at the temperature 1050 °C. The peak on this curve at 300 °C can be explained within the framework of the molecular-field model. This phenomenon will be observed in more detail later on. Samples of a similar type from the X-ray data are two-phase, consisting of hexagonal antiferromagnetic pyrrhotite and monoclinic ferrimagnetic pyrrhotite [8, 9].

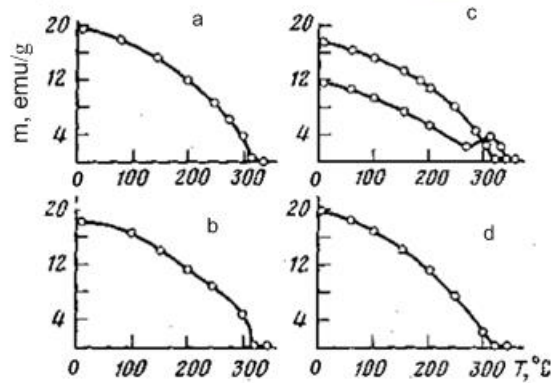


Fig. 2. Dependence of the magnetization on the temperature of pyrrhotites obtained at different pyrite annealing temperatures

### 3. Model representations of a nonstoichiometric ferrimagnet

In a two-sublattice ferrimagnet, part of the ions near which the vacancies are located have a local magnetic field value different from the rest of the ions in the node. This is due to the fact that in the formation of a superstructure, these ions are ordered in a certain way on account of the cation vacancies ordering. Consequently, a two-sublattice ferrimagnet can already be considered as a three-, four-, and so on, sublattice ferrimagnet [10], depending on the type of the vacancy ordering. Such a ferrimagnet will have a number of significant differences from the ordinary two-sublattice ferrimagnet. For example, interactions between sublattices may be missing or may be very small.

For further analysis of the magnetization behavior, it is necessary to consider separately the exchange interaction between cations in a nonstoichiometric ferrimagnet. We can clearly see that in this case it is necessary to take into account not only in which plane the atom is located, but also the first coordination sphere of the given atom crystal structure. Thus, it is necessary to consider at least four types of exchange interaction. We apply to the algorithm described in [10].

Let us denote by  $f, g, k, l$  the nodes of the first, second, third and fourth sublattices.

The quantities related to the first, second, third, and fourth sublattices will be denoted by 1, 2, 3, and 4.

We denote by  $N_i, S_i, \mu_i$  the number of atoms in the sublattice, the magnitude of the spin, and the magnetic moment of the type  $i$  atom.

In general case

$$N_1 \neq N_2 \neq N_3 \neq N_4, \quad S_1 \neq S_2 \neq S_3 \neq S_4, \quad \mu_1 \neq \mu_2 \neq \mu_3 \neq \mu_4, \quad (1)$$

so that the magnetic moments of the sublattices are different.

We write the Hamiltonian system in the form:

$$\begin{aligned} \tilde{H} = & -\mu_1 \sum (H, S_f) - \mu_2 \sum (H, S_g) - \mu_3 \sum (H, S_k) - \mu_4 \sum (H, S_l) - \\ & - \frac{1}{2} \sum I(f_1 - f_2)(S_{f_1}, S_{f_2}) - \frac{1}{2} \sum I(g_1 - g_2)(S_{g_1}, S_{g_2}) - \frac{1}{2} \sum I(k_1 - k_2)(S_{k_1}, S_{k_2}) - \\ & - \frac{1}{2} \sum I(l_1 - l_2)(S_{l_1}, S_{l_2}) - \sum I(f - g)(S_f, S_g) - \sum I(k - l)(S_k, S_l) - \end{aligned}$$

$$-\sum I(g-k)(S_g, S_k) - \sum I(f-k)(S_f, S_k) - \sum I(f-l)(S_f, S_l) - \sum I(g-l)(S_g, S_l), \quad (2)$$

where  $S_f, S_g, S_k, S_l$  are the spin atom operators of the first, second, third and fourth sublattices.

Taking into account the condition for the minimum of free energy:

$$F = -\theta \ln Q, \quad (3)$$

where the partition function:

$$Q = \sum_n e^{-E_n/\theta} = Sp \left( e^{-H/\theta} \right), \quad (4)$$

$\theta = kT$  is the canonical measure module,  $k$  is the Boltzmann constant,  $E_n$  are the eigenvalues of the Hamiltonian  $H$ .

Passing on to the operators

$$S_f^Z, S_g^Z, S_k^Z, S_l^Z, S_f^\pm, S_g^\pm, S_k^\pm, S_l^\pm \quad (5)$$

and applying the Holstein-Primakov-Izyumov representations for spin operators in terms of second quantization operators

$$S_f^+ = \sqrt{2s}\phi(n_f)a_f, \quad S_f^- = \sqrt{2s}a_f^+\phi(n_f), \quad (6)$$

$$S_f^z = S - n_f, \quad (7)$$

$$\phi(n_f) = \left(1 - \frac{n_f}{2S}\right)^{\frac{1}{2}}, \quad (8)$$

$$n_f = a_f^+ a_f, \quad (9)$$

the operators  $a_+$  and  $a$  satisfy the Bose commutation relations.

Assuming that the spins are oriented parallel to each other in each of the sublattices we obtain a system of equations:

$$\begin{aligned} \alpha_1 &= \mu_1 H + J_{11}S_1\sigma_1 + |J_{12}|S_2\sigma_2 + |J_{13}|S_3\sigma_3 + |J_{14}|S_4\sigma_4, \\ \alpha_2 &= \mu_2 H + J_{22}S_2\sigma_2 + |J_{12}|S_1\sigma_1 + |J_{23}|S_3\sigma_3 + |J_{24}|S_4\sigma_4, \\ \alpha_3 &= \mu_3 H + J_{33}S_3\sigma_3 + |J_{32}|S_2\sigma_2 + |J_{13}|S_1\sigma_1 + |J_{34}|S_4\sigma_4, \\ \alpha_4 &= \mu_4 H + J_{44}S_4\sigma_4 + |J_{42}|S_2\sigma_2 + |J_{43}|S_3\sigma_3 + |J_{14}|S_1\sigma_1. \end{aligned} \quad (10)$$

The system of equations represents the required equations of the molecular field for a four-sublattice isotropic ferrimagnet.

$$\begin{aligned} \sigma_1 &= 1 - S_1^{-1} B_{S_1} \left( \frac{\alpha_1}{Q} \right), \\ \sigma_2 &= 1 - S_2^{-1} B_{S_2} \left( \frac{\alpha_2}{Q} \right), \\ \sigma_3 &= 1 - S_3^{-1} B_{S_3} \left( \frac{\alpha_3}{Q} \right), \\ \sigma_4 &= 1 - S_4^{-1} B_{S_4} \left( \frac{\alpha_4}{Q} \right); \end{aligned} \quad (11)$$

$$M^z = M_1^z + M_2^z + M_3^z + M_4^z; \quad (12)$$

$$M_i = N_i S_i \mu_i \sigma_i, \quad (13)$$

where  $\sigma_i$  is a fractional magnetization per one node in the sublattice.

Fig. 3 shows the calculated temperature dependences each of the 4 sublattices, which were defined from an equation (12), and also the curves of the summarized magnetization considering two and four sublattices. In more detail, the magnetization dependence of certain sublattices and the ratio exchange on sublattices is observed in [11].

Fig. 4 shows the possible temperature changes in the magnetization of the samples in case if the dependence of the sublattices exchange integrals on the number of certain sublattices vacancies is taken into account. The corresponding changes in the magnetizations of each sublattice are shown in Fig. 4 (A, B). It is seen from the presented graphs that the abstract curve 1 (Fig. 4C) goes with the experimental dependence of the change in magnetization on the temperature, which is demonstrated in Fig. 2c. The peculiarity of this dependence is that the magnetization is raised nearly to the Curie temperature. The abstract curves can also be used to describe other experimental dependences of  $m(T)$ .

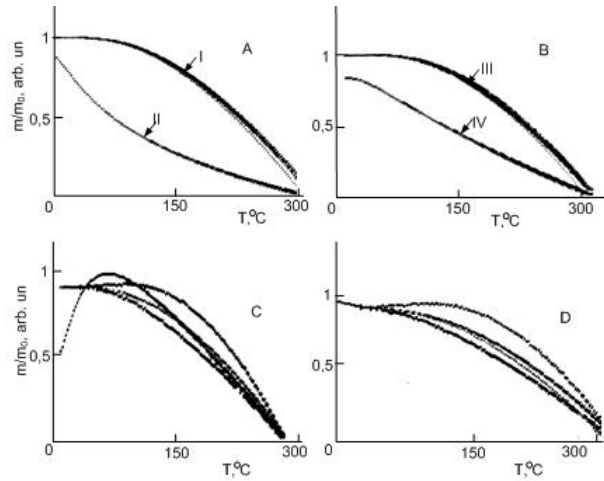


Fig. 3. Calculated temperature dependence of the magnetization each of the four sublattices (A and B) and the summarized magnetization considering two (C) and four (D) antiferromagnetic sublattices

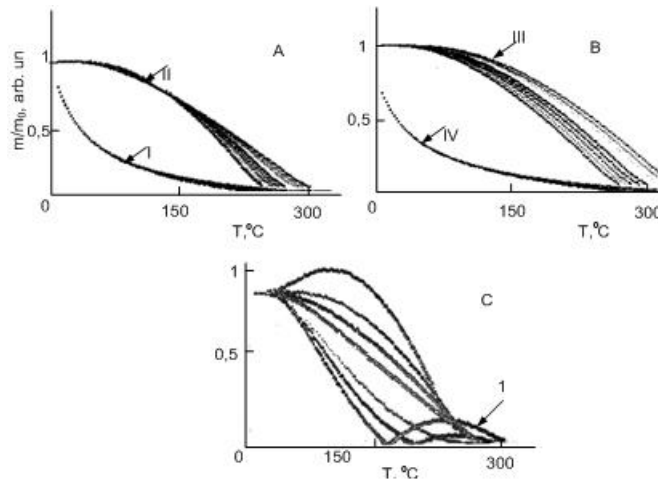


Fig. 4. Possible types of  $m/m_0(T)$  curves for each of the sublattices (I–IV) and the summarized magnetization (C) in case if the number of vacancies varies with the temperature

## Conclusion

Thus, the proposed theoretical description of a nonstoichiometric ferrimagnet as a four sublattice allows qualitatively to explain its magnetic properties. This provides opportunities in predicting the magnetic properties of chalcogenides containing point defects in the crystal structure. A connection was found between the type of vacancy distribution and the magnetic properties of non-stoichiometric ferrimagnets such as pyrrhotite. Within the framework of the molecular-field approximation, a theoretical explanation was given to the dependence of the magnetization on the temperature of magnetically ordered compounds containing cation vacancies in the crystal structure. On the basis of the proposed model of the vacancy behavior, the theoretically possible dependences of the magnetization on the temperature were presented.

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## Возможные типы упорядочения катионных вакансий в структурах типа NiAs

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*Установлена связь между типом распределения вакансий и магнитными свойствами нестехиометрических ферримагнетиков типа пирротина. В рамках приближения молекулярного поля дано теоретическое объяснение зависимости намагниченности от температуры магнитоупорядоченных соединений, содержащих катионные вакансии в кристаллической структуре. На основе предложенной модели поведения вакансий представлены теоретически возможные зависимости намагниченности от температуры.*

*Ключевые слова: пирротин, пирит, кристаллическая структура, катионные вакансии, фазовый состав, ферримагнетик.*