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Magnetization of a Pyrrhotite of Composition $Fe_{0.847}S$ in Area of a Curie Point

Viktor V. Onufrienok* and Anatoly M. Sazonov

Siberian Federal University,
79 Svobodny, Krasnoyarsk, 660041 Russia [1]

The x-ray, Mossbauer and termomagnetic researches of pyrrhotites possessing high-temperature λ − peak (T_λ = 310 °C) on curve dependence of magnetization on temperature − I (T) are lead. The chemical compound and conditions of formation of such pyrrhotites is determined. It is established, that samples with λ − peak possessed the raised maintenance of sulfur in comparison with pyrrhotites Fe_7S_8 and corresponded to structure $Fe_{1-n}S$ (n=0.153). As has shown experiment, these pyrrhotites are in a metastable phase condition and in due course (samples were observed during 29 years) pass in a pyrite and a pyrrhotite of structure Fe_7S_8 (at the presence of an atmosphere the Goethite and a szomolnokit was formed also). Because of quantum-mechanical calculations of dependence of specific magnetization from temperature for various under-lattices with various integral of exchange interaction good conformity of a settlement curve with experimental is received. Calculations were made within the framework of model of a molecular field for a two-sublattice ferrimagnetic.

Keywords: the pyrrhotite, a metastable phase, a szomolnokit, quantum-mechanical calculations, spin, ferrimagnetic, a molecular field, magnetization.

Introduction

One of carriers of magnetism of rocks is the pyrrhotite (sulfides of iron Fe_{1-n} S ($0 < n < 0.125$), possessing structure such as NiAs) [1].

Magnetic properties of this mineral are in direct dependence on its history of formation, therefore their studying is interesting to understanding of some problems of geomagnetism. These properties of pyrrhotites are in direct dependence on temperature, pressure, crystal structure, a chemical compound, and also on type of distribution of cationic vacancies on magnetic sublattice (i.e. from superstructure) [3,7-9].

The pyrrhotite possesses structure with weak distortions in which the part of cationic positions is vacant [1]. Hence, the mineral is similar to a form solution of cationic vacancies in pseudo-hexagonal crystal structure. It is obvious, what even at a constant chemical compound the type of distribution of vacancies can influence physical properties of a mineral essentially. In turn, distribution of vacancies in structure depends on any sort of external influences and time [3,7-9].

Formation of cationic vacancy breaks an electric neutrality of a molecule. There is a subsequent nationalization of valent electrons and formation of distinct from zero of average on time of a negative charge for vacant unit. The electric field on vacant unit also is responsible for interaction between vacancies. Partly therefore metastable minerals at a constant chemical compound and external thermodynamic parameters can pass their one superstructure in another, do not achieve yet to a minimum of free energy [2,5]. It is obvious, that if external conditions change, distributions of vacancies in structure also can change. The distribution of cationic vacancies is directly connected to magnetic properties of minerals we shall note [1, 7-9].

At research of termomagnetic properties of artificial pyrrhotites on curve magnetization it can be observed λ – peak. We shall notice, that λ – the peak on curve dependence I/I_0 (T) at pyrrhotites is observed at various temperatures depending on a chemical compound and conditions of formation [3, 7]. For example, λ – the peak on curve magnetization I/I_0 (T) (T_λ = 160 °C) at structure $Fe_{1-n}S$ (n=0.099) occurs is a result of redistribution of cationic vacancies in basic planes of crystal structure. The λ – peak of magnetization (T_λ = 275 °C) at structure $Fe_{1-n}S$ (n=0.091) is a result of redistribution of vacancies along a crystallographic axis "c" [5, 7, 8]. However λ – the peak of magnetization at artificial pyrrhotites (T_λ = 310 °C) until now up to the end is not investigated, though in the literature there is a mention of this effect [3].

The purpose of work: to determine conditions of formation and a chemical compound of the pyrrhotites possessing high-temperature (T_λ = 310 °C) λ – peak on curve I/I_0 (T). Establish the nature of this phenomenon based on researches by x-ray methods and methods γ – resonant spectroscopy to. Representations a theoretical substantiation of the nature high-temperature λ – peak to offer based on quantum-mechanical.

Samples

Samples for researches prepared various methods. One series (a series "A") samples have been received by a method of dry synthesis because of sintering settlement quantity of sulphur and iron in vacuum in quartz ampoules at temperature 1000 °C. Some of samples of this series were exposed to a hardening in liquid nitrogen, and other part was slowly cooled up to temperature 20 °C with a speed of 10°/minutes. Pyrrhotites of a series "Б" turn out because of an annealing in 2/3 hours of a natural pyrite (FeS_2) in vacuum at temperatures from 400 up to 1000 °C. The pyrite was located in a long quartz tube with pumping out of atoms of gaseous sulfur, stripping of a pyrite at heating. Samples of a series "Б" also would be cooled by various images. The part of samples was has tempered in flowing water up to temperature 14 °C, and other part is cooled with a speed of 10 °/minutes up to temperature 20 °C. Accepting artificial, natural pyrrhotite of a various chemical compound (a series "B") were has investigated also.

Experiment

All samples then were has exposed to x-ray research of structure on diffractometer DRON-3 with radiation Co (K_α-radiation) and to the analysis of magnetic properties on thermoballistic installation in a field 1000 oersted. Mossbauer of spectra was has removed with source Co^{57} in matrix Cr.

As a result of researches it is established, that high-temperature λ – the peak on curves I/I_0 (T) is characteristic for samples of series "A" and "Б", and in natural minerals was has not observed. We shall
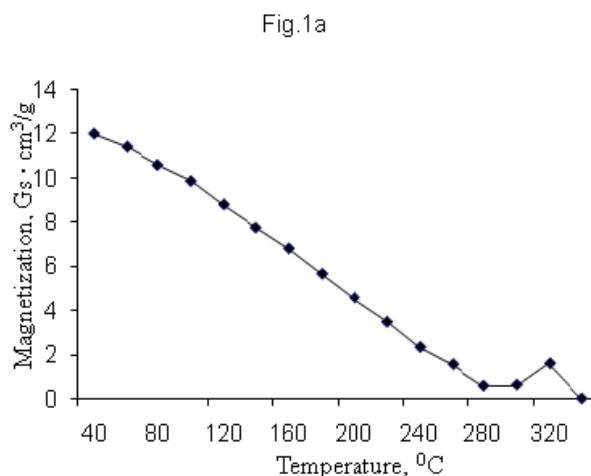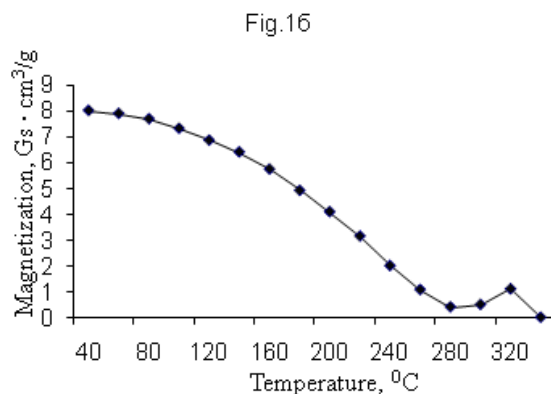
Fig.1б

Fig.1a

Fig. 1. Dependence of relative magnetization on temperature of pyrrhotites: (б) – synthesized at 1000 °C in vacuum; (a) – as a result of thermal decomposition in vacuum of a pyrite at t=700 °C

notice, that in the literature also there are no data on natural pyrrhotites with similar properties though for artificial samples given λ − the peak on curve I/I_0 (T) was already marked [3]. It is possible to conclude, that this phenomenon is typical only of pyrrhotites in a metastable phase condition. On Fig. 1 dependences of magnetization (I) from temperature (T) samples of a series "A" and are submitted to a series "Б".

For these samples typically presence λ − peak on curve of magnetization I (T). The first sample is synthesized at temperature 1000 °C the subsequent a hardening (Fig. 1б), and the second sample is received as a result of an annealing of a pyrite in vacuum at temperature 1000 °C and also tempered then from this temperature. The chemical compound of samples with λ − peak on curve magnetization I (T) was has defined by the x-ray method offered Arnold [10] с by account of comparative correction factors. Appeared, that researched samples with λ − peak on curve magnetization I (T) are more enriched with ions of sulfur, in comparison with natural pyrrhotites Fe_7S_8. If in natural samples on each ion of iron 1,14 ions of sulfur in the received samples of sulfur contained approximately 1,18 on each ion of iron can have. Thus the chemical compound of pyrrhotites with λ − peak on curve magnetization I (T) can be submitted by formula Fe_{1-n} S (n=0.152). It is necessary to note, that λ − the peak at temperature 275 °C is observed at natural pyrrhotites of structure $Fe_{1-n}S$ (n=0.091) [7], hence high-temperature λ −
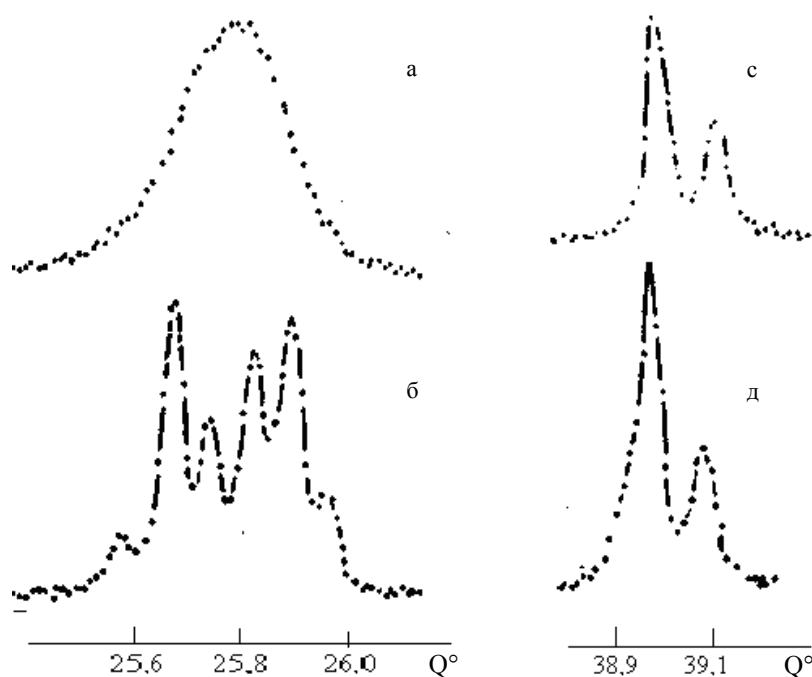
Fig 2. The Structure of a reflex (102) pyrrhotites: (a) – with high-temperature λ – peak; (б) – natural pyrrhotite Fe_7S_8. X-ray reflexes (004): (c) – pyrrhotites of structure $Fe_{1-n}S$ (n=0.152); (д) – a natural pyrrhotite of structure Fe_7S_8

the peak cannot be simply displaced λ – peak of samples of a series "In" as possesses distinct from the first λ – peak properties and is characteristic for other chemical compounds.

On Fig.2a the structure of a reflex (102) pyrrhotites with high-temperature λ – peak is submitted, and on Fig.2б a structure of the same x-ray reflex of a natural pyrrhotite with $Fe_{1-n}S$ (n=0.12) .

Этот the X-ray reflex is maximum susceptible to syngonies of a pyrrhotite. The natural pyrrhotite of this structure did not possess λ – peak on curve magnetization I (T) and has monoclinic crystal structure (an axis "c" has a deviation from 90°) [1]. On Fig. 3a and Fig. 3б are submitted x-ray a reflex (004) pyrrhotites of structure $Fe_{1-n}S$ (n=0.152) and a natural pyrrhotite of structure $Fe_{1-n}S$ (n=0.12) accordingly. This x-ray reflex is maximum susceptible to internuclear distances along an axis "c" a pyrrhotite.

The analysis of the submitted x-ray reflexes allows to assume, that the crystal structure of pyrrhotites of structure $Fe_{1-n}S$ (n=0.152) is deformed. Internuclear distances between ions of iron in basic planes (along an axis "a") have wide disorder of values while along an axis "c" internuclear distances are practically constant and equal 2,83 Å both at natural, and at artificial pyrrhotites. The crystal structure is in an unstable power condition and free energy of her is has not minimized. Concentration of vacancies in an elementary cell of artificial pyrrhotites exceeds maximum permissible value for a stable phase condition.

On rice 4a the spectrum of the Mossbauer of monoclinic natural pyrrhotite Fe_7S_8, and on Fig. 4б – a pyrrhotite of structure $Fe_{1-n}S$ (n=0.152) with λ – peak on curve magnetization I (T) is submitted.

Spectra were has removed at temperature of liquid nitrogen for the best sanction of sextuplets. In the first case the spectrum of the mossbauer of a monoclinic pyrrhotite will consist of three
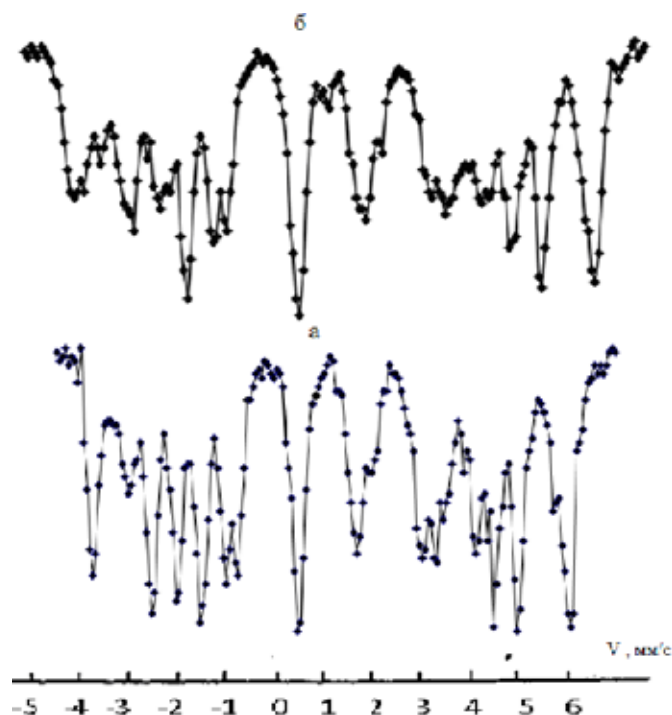
Fig 3. The Spectrum of the nuclear γ- resonance: (a) – natural pyrrhotite Fe_7S_8; (б) – the synthesized pyrrhotite of structure Fe_{1-n} S (n=0.152) with λ – peak on curve magnetization I (T)
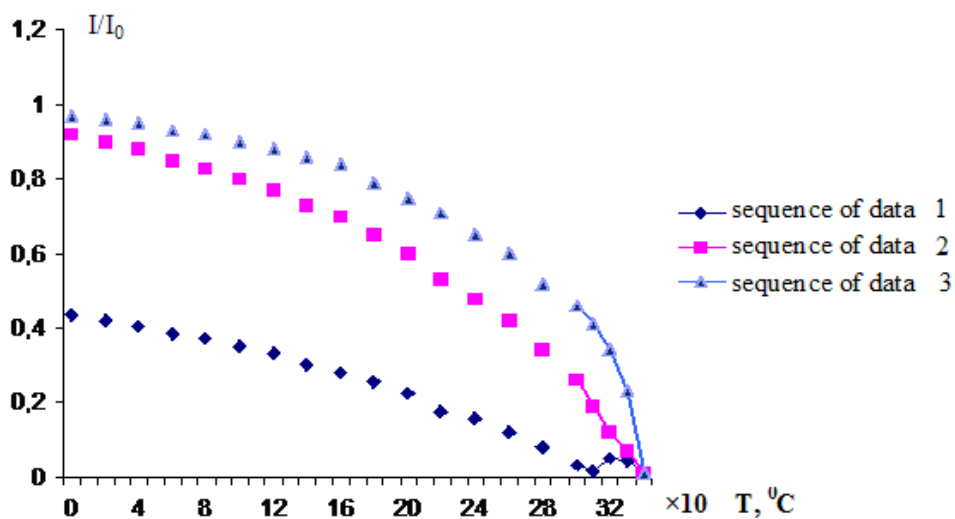

Fig. 4. Dependence of relative magnetization on temperature. The first sublattice (sequence of data 3) with exchange integral $J_{11} = 8.41 \cdot 10^{-21}$ Joules. The second sublattice (sequence of data 2) with exchange integral. $J_{22} = 4.19 \cdot 10^{-21}$ Joules. A sequence of data 3 – resulting magnetization

resolved sextuplets corresponding to values of magnetic fields on nucleus of three under-lattices, equal 24032, 20212, 18064 A/m. These values of local magnetic fields correspond to positions of ions of iron without vacancies, with two vacancies and four vacancies in the second coordination sphere accordingly [7-8]. Such positions of ions of iron can arise only in the event that vacancies are located only in even or odd basic planes. The analysis of these spectra allows concluding, that in this condition cationic vacancies are has ordered in even (odd) basic planes. It corresponds to structural transition B8-C6 in an intermediate stage. Calculation of population of positions in this structure gives $N_0 = 0,47$; $N_1 = 0$, $N_2 = 0,39$, $N_3 = 0$; $N_4 = 0,23$. We shall note, that vacancies at the casual law of distribution should have population $N_0 = 0,21$, $N_1 = 0,3$, $N_2 = 0,31$, $N_3 = 0,14$, $N_4 = 0,05$ (N_0, N_1, N_2, N_3, N_4 – population of positions without vacancies, with one vacancy, two, three and four vacancies accordingly).

In spectra of the Mossbauer of pyrrhotites with λ – peak on curve magnetization I (T) there is no precise sanction of these sextuplets though it is possible to conclude, that positions of ions of iron with two, to four and without vacancies obviously are present. It is possible to assume also from the analysis of a spectrum, that except for the specified positions there are positions with one and three vacancies at the second coordination sphere. Processing of a spectrum of a pyrrhotite forces to assume presence of additional sextuplets in this spectrum. Satisfactory there approximated a spectrum by five sextuplets with sizes of fields: 24032, 22120, 20212, 19513, 18064 A/m. cations in such structure have accordingly 0,1, 2, 3 and 4 vacancies in the second coordination sphere. Calculation of population of positions in an initial condition of the tempered samples is given with values $N_0 = 0,41$, $N_1 = 0,10$, $N_2 = 0,25$, $N_3 = 0,08$, $N_4 = 0,17$. The obvious deviation of distribution of vacancies from the casual law is has observed.

The estimation of population was has made under the analysis of relative intensity of sextuplets on which the experimental spectrum of the Mossbauer decayed. These populations were compared with expected for the casual law of distribution.

Thus, vacancies in structure of a pyrrhotite of structure $Fe_{1-n}S$ (n=0.152) are not located only in even or odd basic planes and what – that their part is in the disorder condition. The partial missequencing of vacancies reduces the total magnetic moment of under-lattices as in each of under-lattices ferromagnetic spin ordering is realized, and between them – antiferromagnetic [1]. Thus, though samples with λ – peak on curve magnetization I (T) are more enriched with ions of sulfur in comparison with a monoclinic pyrrhotite, nevertheless possess smaller value of specific magnetization.

It is necessary to note, that as a result of an annealing in vacuum of samples of structure $Fe_{1-n}S$ (n=0.152) at temperature 350 °C during one hour with the subsequent slow cooling with a speed in 1 °/minutes up to temperature 20 °C pyrrhotites with monoclinic crystal structure of structure $Fe_{1-n}S$ (n=0.12) in balance with a pyrite turned out. Magnetization of the samples received as a result of an annealing grew and reached 18 Gs ·см³./g at temperature 20 °C though up to an annealing did not exceed 12 Gs · sm³/g.

From the analysis of the experimental facts it is possible to conclude, that λ – the peak on curve dependence I(T) at temperature 310 °C to not speak ordering of vacancies in basic planes or between basic planes along a crystallographic axis "ß". It cannot be explained also phase transition of a pyrrhotite in monoclinic structure. Really, the monoclinic pyrrhotite can exist only up to 290 °C, and λ – the peak is observed at temperature 310 °C. Thus, neither distribution of vacancies to magnetic under-lattices,

nor symmetry of an elementary cell at λ − a pique does not change. Hence, it is necessary to assume, that λ − the peak on curve dependence I (T) is consequence of features of exchange interaction of the magnetic under-lattices, caused by type of distribution of cationic vacancies on them.

Methods of calculation of defects

For the analysis of dependence of magnetization from temperature of each of sublattice, and also magnetizations of a crystal, have been applied a method of a molecular field for the two-sublattice ferrimagnetic to [6,11] structure of pyrrhotites in a metastable phase condition.

Let's designate through f, g, the units of first and second sublattice. The size of concerning to first and second sublattice, we shall designate 1 and 2. Through N_i, S_i, μ_i we shall designate numbers of atoms in a sublattice, size a spin and the magnetic moment of atom of a grade i.

Generally

$$N_1 \neq N_2, \ S_1 \neq S_2, \ \mu_1 \neq \mu_2$$

so the magnetic moments of sublattice are various.

Resulting magnetization

$$M^z = M_1^z + M_2^z$$

where

$$M_i = N_i S_i \mu_i \sigma_i$$

σ_i − relative magnetization on one unit in a sublattice i.

We shall write down a Hamiltonian of system as:

$$\widetilde{H} = -\mu_1 \sum \left(H, S_f\right) - \mu_2 \sum \left(H, S_g\right) - \frac{1}{2} \sum I\left(f_1 - f_2\right)\left(S_{f_1}, S_{f_2}\right) -$$

$$- \frac{1}{2} \sum I\left(g_1 - g_2\right)\left(S_{g_1}, S_{g_2}\right) - \sum I\left(f - g\right)\left(S_f, S_g\right)$$

Where S_f, S_g, − spin operators of atoms of the first and second sublattice, H − an external magnetic field.

Considering a condition of a minimum of free energy: $F = -\vartheta \ln Q$

Where the statistical sum:

$$Q = \sum_n \exp\left(-E_n / \vartheta\right) \ = Sp\left(\exp\left(-\frac{\widetilde{H}}{\vartheta}\right)\right)$$

where E_n − own values of a Hamiltonian $\widetilde{H}$ and taking into account, that the module of initial distribution is equal: $\vartheta = \kappa T$

Having assumed, that in each of sublattice of a spin are focused in parallel each other, we shall receive system of the equations

$$\left.\begin{array}{l} \alpha_2 = \mu_2 H + J_{22} S_2 \sigma_2 + \left|J_{12}\right| S_1 \sigma_1 \\ \alpha_1 = \mu_1 H + J_{11} S_1 \sigma_1 + \left|J_{12}\right| S_2 \sigma_2 \end{array}\right\}$$

The system of the equations also represents the required equations of a molecular field for a two-sublattice isotropic ferrimagnetic. Relative magnetization of ions of iron for each of sublattice will be defined by the equations:

$$\sigma_1 = 1 - S_1^{-1} B_{S_1}\left(\frac{\alpha_1}{Q}\right)$$

$$\sigma_2 = 1 - S_2^{-1} B_{S_2}\left(\frac{\alpha_2}{Q}\right)$$

where

$$B_{S_i}\left(\frac{\alpha_i}{Q}\right) - function\ Brillouin$$

Resulting magnetization of a crystal is caused by various distributions of cationic vacancies to sublattice. Calculations of magnetization of nonstoichiometric sulfides of iron have been lead at various temperatures and with various values of exchange integrals.

On Fig. 4 settlement dependences of magnetization on temperature are submitted: the curve of dependence of relative magnetization sublattice with smaller value of exchange integral more flat (sequence of data 2 on Fig. 5), than a curve sublattice with great value of exchange integral.

It is obvious, that cationic vacancies, settling down mainly on one of sublattice, change average values of exchange integrals on this sublattice. Apparently from Fig. 4, it changes character of dependence I/I_0 (T) for each of sublattice. As the size of full magnetic energy of a crystal does not change (on a condition), the temperature of transition of a sample in a paramagnetic condition remains constant, equal 340 °C. We shall notice that the total magnetic moment of each of sublattice depends on concentration of cationic vacancies on it. In result, the more vacancies it is concentrated mainly on one of sublattice, the it is more and magnetization of a sample.

As a first approximation, we shall consider two magnetic sublattice with an antiparallel direction спинов in everyone and excellent at each of sublattice of the total magnetic moment and integral of exchange interaction. The analysis of dependence of specific magnetization from temperature of each of sublattice within the framework of model of a molecular field has shown that if the exchange integral is less at sublattice with great value of the magnetic moment she has more abrupt recession (Fig. 4, sequence of data 3) near to temperature of the Curie. As a result of it in some point, total magnetization of sublattice will address in a zero, and then some increase in magnetization (Fig. 4, sequence of data 1) will follow. On Fig. 4 curve dependences of specific magnetization on temperature sublattice with exchange integral J_{11} = 8.41 · 10^{-21} Joules are submitted (sequence of data 3) and under-lattices with exchange integral J_{22} = 4.19 · 10^{-21} Joules (sequence of data 2). Exchange integral between sublattice there were equal J_{12} = J_{21} =6.11 · 10^{-21} Joules. Let's notice, that exchange integrals were defined by a method of a molecular field in view of the experimental facts. From Fig. 4 (sequence of data 1), it is visible, that the curve of total magnetization near to temperature of the Curie has λ − peak on curve dependence of specific magnetization on temperature. For presentation this curve of magnetization is normalized not on unit, and on 0,5. We shall notice, that λ − the peak on curve dependence of specific magnetization is caused only by distinction of exchange integrals of magnetic sublattice. This difference exchange interaction can be caused by the superfluous ions of sulfur introduced into crystal structure and, as consequence, deformations of this structure. Ions of sulfur can delay on themselves
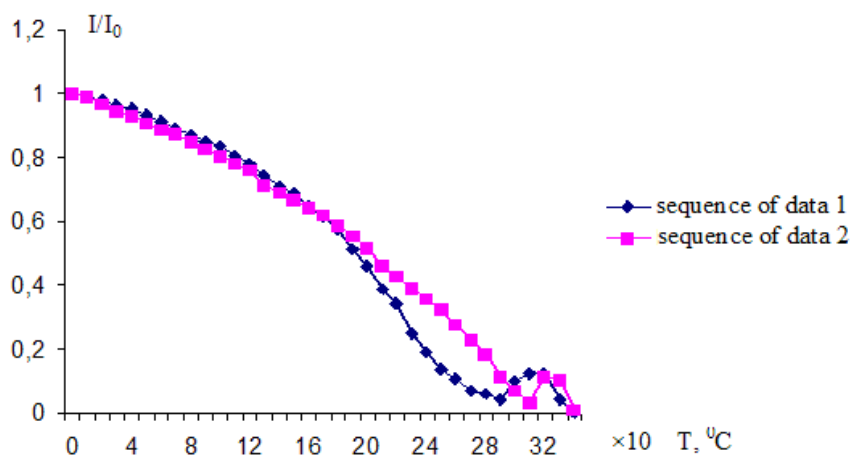
Fig. 5. Dependence of magnetization on temperature. settlement curve (sequence of data 2) experimental curve (sequence of data 1)

a part of ions of iron, creating additional cationic vacancies those results in turn in displacement from equilibrium conditions of other ions of iron. These displacement can be excellent on sublattice, hence, can differ and a configuration of electronic orbits, as results in a result in difference on sublattice of exchange interaction. Clearly, that such structure does not possess a minimum of free energy, therefore at transition of a pyrrhotite in a stable phase condition λ – the peak on curve dependence I (T) vanishes. It was reached as a result of an annealing of samples during one hour at temperature 350 °C. On Fig. 5 conformity of a settlement curve (sequence of data 2) with experimental (sequence of data 1) is submitted.

We shall notice, that this phenomenon (λ – the peak on curve dependence of specific magnetization on temperature) experimentally was revealed earlier, however had no explanation. Within the framework of the offered method, this result turns out naturally. On Fig. 5 this dependence is submitted, and for comparison, the experimental curve is shown. Though some divergence between settlement and experimental curves is observed, nevertheless, they are in good enough qualitative conformity.

Conclusions

As a result of the lead researches conditions of formation of pyrrhotites with high-temperature λ – peak on curve dependence I (T) (synthesis in vacuum are established at 1000 °C with following a hardening of samples), and their chemical compound – _Fe$_{1-n}$S (n=0.152) is determined. As has shown experiment, these pyrrhotites are in a metastable phase condition and in due course (samples were observed during 29 years) pass in a pyrite and a pyrrhotite of structure Fe$_7$S$_8$ (at the presence of an atmosphere the goethite and a szomolnokit [4] was formed also). From the analysis of Mossbauer spectra, it is possible to conclude, that vacancies of ions of iron are in structure in part in a missequencing condition, as results in reduction of relative magnetization of initial samples. The mechanical calculations lead a quantum within the framework of model of a Two lattices Ferrimagnetic have shown, that λ – the peak on curve dependence I (T) can be result of distinction of exchange integrals of magnetic under-lattices. This distinction speaks ordering of cationic vacancies mainly in even basic planes of crystal structure. Good enough conformity of the theory with experiment is has received.

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Намагниченность пирротина состава $Fe_{0.847}S$
в районе точки Кюри

В.В. Онуфриенок, А.М.Сазонов

Сибирский федеральный университет,
660041 Россия, Красноярск, пр. Свободный, 79

Проведены рентгеновские, мессбауэровские и термомагнитные исследования пирротинов, обладающих высокотемпературным λ-пиком ($T_λ$ = 310 °С) на кривой зависимости намагниченности от температуры – I (T). Определен химический состав и условия образования таких пирротинов. Установлено, что образцы с λ-пиком обладали повышенным содержанием серы по сравнению с пирротинами Fe_7S_8 и соответствовали составу $Fe_{1-n}S$ (n=0.153). Как показал эксперимент, эти пирротины находятся в метастабильном фазовом состоянии и со временем (образцы наблюдались в течение 29 лет) переходят в пирит и пирротин состава Fe_7S_8 (в присутствии атмосферы образовывался также гетит и самольнокит). В результате квантово-механических вычислений зависимости удельной намагниченности от температуры

для различных подрешеток с различным интегралом обменного взаимодействия получено хорошее соответствие расчетной кривой с экспериментальной. Расчеты производились в рамках модели молекулярного поля для двухподрешеточного ферримагнетика.

Ключевые слова: спин, пирротин, пирит, самольнокит, двухподрешеточный ферромагнетик, молекулярное поле, намагниченность.