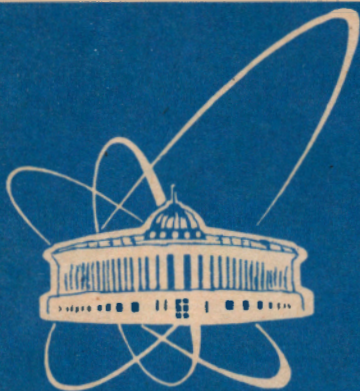


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СООБЩЕНИЯ
ОБЪЕДИНЕННОГО
ИНСТИТУТА
ЯДЕРНЫХ
ИССЛЕДОВАНИЙ

Дубна

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STRUCTURAL TRANSFORMATIONS
IN NATURAL GELS
ACCORDING TO RESONANCE METHODS DATA

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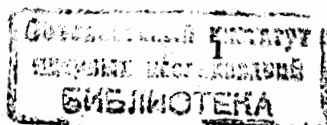
In recent years growing interest has developed in the study of glasses with high iron concentration [1,2]. From this point of view the interest to natural colloids of alumo-ferrous-sulphate-phosphate composition is increasing, too. The Fe_2O_3 content in these colloids changes from 0.5% to 60%. Besides, the natural colloids are mineral forming systems in which the crystallization of various minerals takes place: from liquid alumo-ferrous-sulphate-phosphate hydrosols to solid gels of the same composition and finally to crystal sulphates and phosphates. The studied colloids are liquids of yellow, yellow-brown and dark-brown colour and different composition. Solid glass-like gels appear from coagulation of hydrosols.

In this work the natural solid gels of next composition:

1. $(\text{Al}_{2.0}\text{Fe}_{0.1})_3[(\text{PO}_4)_{0.5}(\text{SO}_4)_{0.5}]_{0.5}(\text{OH})_8 \cdot 6\text{H}_2\text{O}$
2. $(\text{Al}_{1.0}\text{Fe}_{2.1})_3[(\text{PO}_4)_{0.8}(\text{SO}_4)_{0.2}]_2(\text{OH})_4 \cdot 6\text{H}_2\text{O}$

were studied by EPR, NMR'H and Mössbauer spectroscopy methods. Two groups of samples have different content of mineral forming metals: in the first group aluminium makes up the most part of the composition, in the second one iron plays an important role. The Fe_2O_3 content in gels of the first group changes from 0.5% to 5%.

The EPR-spectra were obtained at 98 GHz on an "Bruker" spectrometer with a temperature controller ranging from 73 K to 473 K. They show similar features: the sharp line that appears at $g=4.3$ is characteristic of isolated Fe^{3+} in octahedral environment of six oxygen anions and the broad line at $g=2$ caused by impurities and hyperfine octet of VO^{2+} (see fig.1).



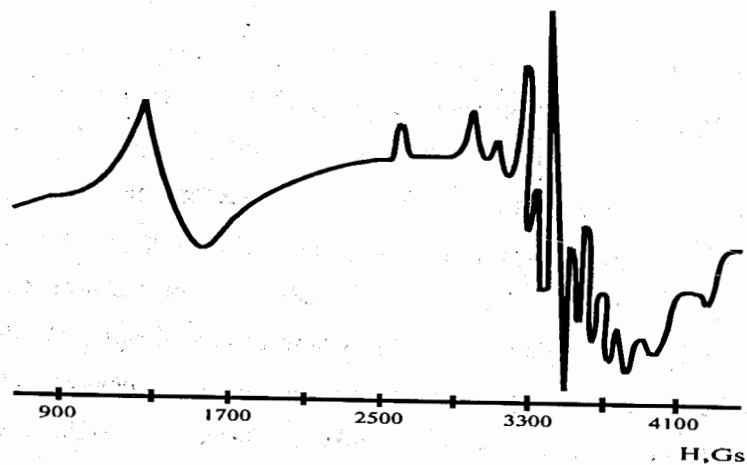


Fig.1. EPR-spectrum of gel of the first group.

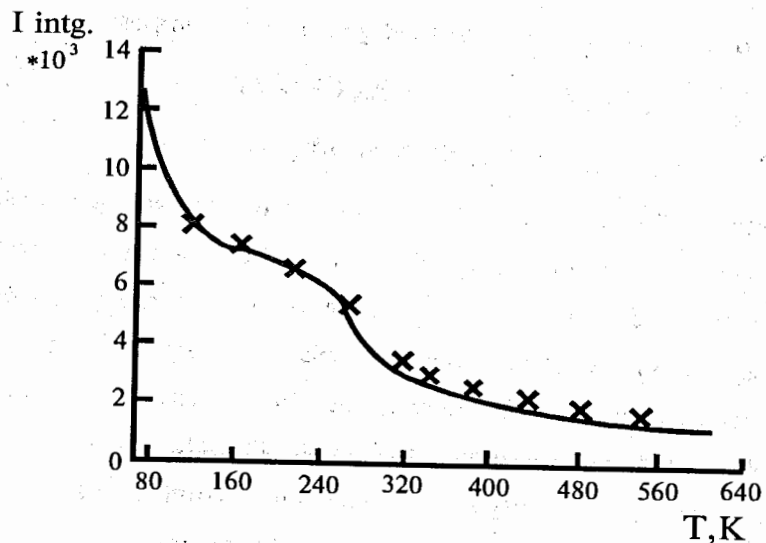


Fig.2. Temperature dependence of the intensity of EPR-line at $g=4.3$.

For gels containing 0.5...5% Fe_2O_3 temperature variation of integrated intensity of line at $g=4.3$ is plotted in figure 2. An abrupt change in intensity of EPR signal caused by Fe^{3+} in octahedral coordination is observed in the temperature range 215...240 K. It can be associated with the change of Fe^{3+} ion's environment in gels.

To determine the type and the content of oxygen-hydrogen groups in gels, the NMR'H method was used. NMR-spectra were recorded on the wide line spectrometer Tesla BS 487B with work frequency 70 MHz. The results of analyses of low-temperature NMR'H spectra for gels of the first group are shown in table 1, where N and N_{xx} are the full water content and the OH-groups amount in 100g of substance.

Table 1. The results of analyses of NMR'H spectra for gels of the first group.

T,K	298	383	473	573	683
N^*	2.78	2.18	1.62	1.39	1.07
$P_{OH}, \pm 0.02$	0.20	0.27	0.49	0.47	0.67
$P_{H_2O}, \pm 0.02$	0.67	0.62	0.51	0.53	0.33
$P_{H_3O^+}, \pm 0.02$	0.13	0.11	0.00	0.00	0.00
$N_{OH}, \pm 0.10$	1.10	1.20	1.50	1.30	1.40
$N_{H_2O}, \pm 0.05$	1.86	1.35	0.83	0.65	0.35
$N_{H_3O^+}, \pm 0.05$	0.24	0.16	0.00	0.00	0.00
$R_{OH}, \pm 0.10 A$	1.30	1.40	1.50	1.50	1.40
$R_{H_2O}, \pm 0.10 A$	1.60	1.60	1.66	1.66	1.66
$R_{H_3O^+}, \pm 0.10 A$	1.72	1.72	-	-	-

It can be seen from table 1, 18% of protons form acidic H_3O^+ groups in air-dry sample. As after annealing of sample at 373K $N_{H_3O^+}$ equals zero, N_{OH} increases and full OH-groups content doesn't change, it can be confirmed that H_3O^+ - groups appear in gels like wavellite from short hydrogen bond between proton of OH-group and neighboring water molecule [3].

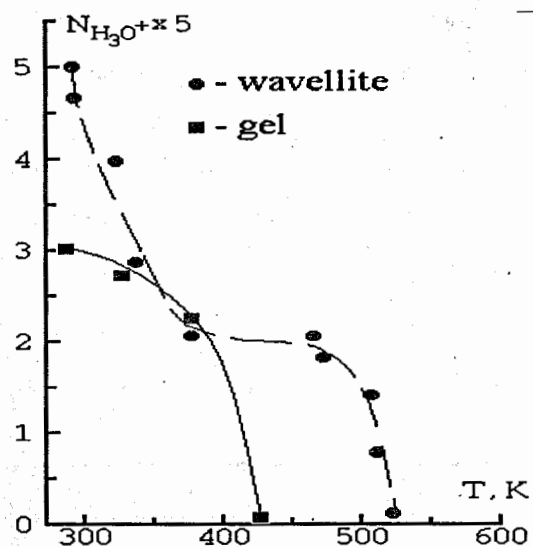


Fig.3. Dependence of the H_3O^+ - groups amount from the temperature annealing.

It is seen from figure 3 that three-spin proton configurations are more stable in wavellite than in gels. Their destruction is observed in temperature interval 470...520 K for wavellite and for gels the later is 380...420 K. The temperature variations of NMR'H spectra of gels in the range 215...240 K show their strong narrowing caused by appearance of translation mobility of H_3O^+ groups (fig.4).

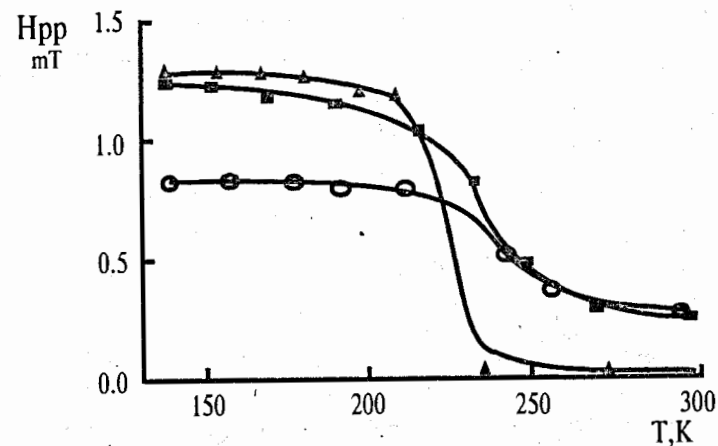


Fig.4. Temperature dependence of the width of NMR'H line.

On the other hand the destruction of acidic H_3O^+ groups at 380...420 K is accompanied by transformation of structural polyhedra according to EPR and Mössbauer data (see below).

Thus, in the gels of the first group mobility and stability of acidic H_3O^+ groups play an important role.

For gels of the second group containing 10...20% of Fe_2O_3 the EPR-spectra are characterized by broad and sharp lines at $g=2$ (fig.5).

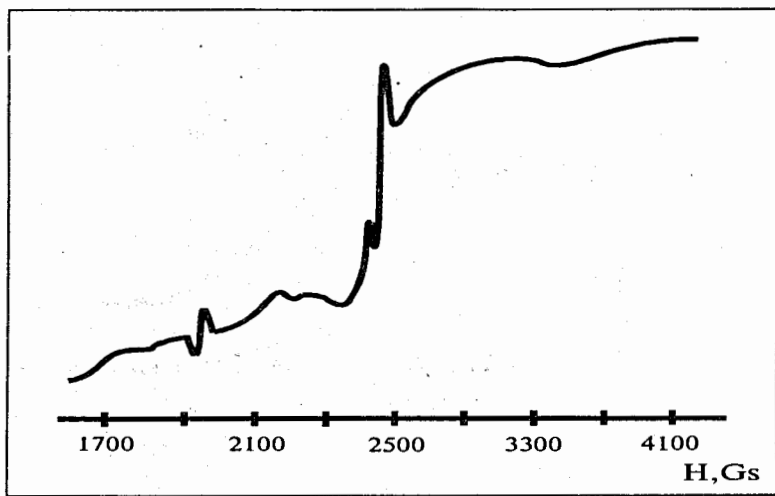


Fig.5. EPR-spectrum of gel of the second group.

The width of the first line changes from 458 G to 800 G for these concentrations of Fe_2O_3 and the other line narrows (ΔH_2 changes from 125 G to 80 G). Rather, the different widths are caused by various symmetries of Fe^{3+} environment or by various aggregate states of iron.

The comparison of EPR-spectra of iron in glasses and gels shows their likeness. Many authors [4] analyzing EPR-spectra in glasses conceive that the number of non-equivalent states of iron is more in glasses than in crystals and these states are distorted in glasses more strongly.

After annealing of samples at 383 K the intensity of the broad line changes essentially and at 873 K it disappears.

To specify the position of Fe^{3+} ions the Mössbauer spectra of the gels were obtained using a constant acceleration spectrometer with $^{57}\text{Co}(\text{Cr})$ source (see fig.6).

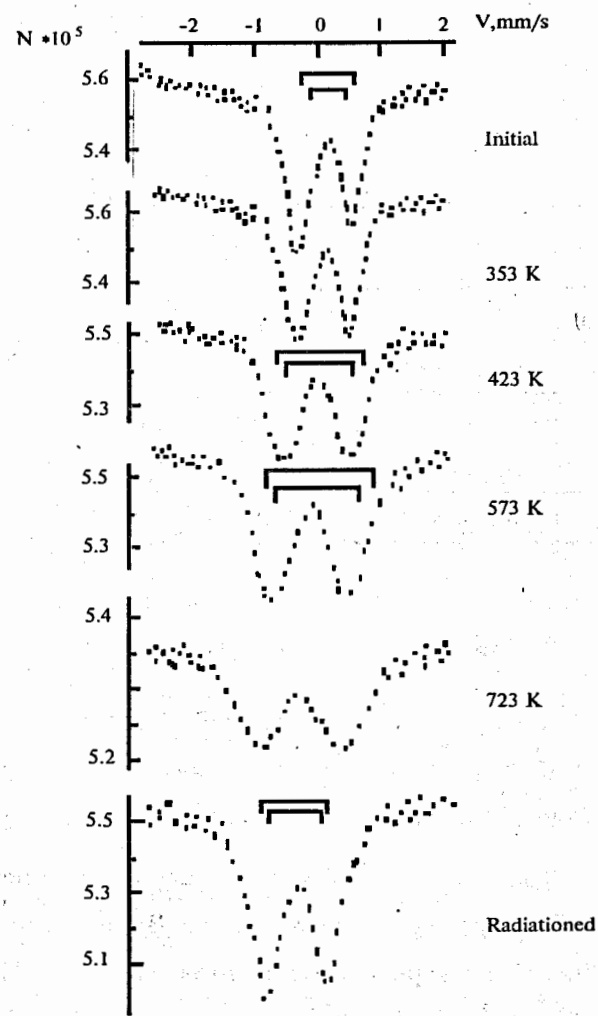


Fig.6. Mössbauer spectra of gel containing 14% of Fe_2O_3 and their change after annealing of samples.

The least square fitting procedure was used for the analysis of the spectra. The received Mössbauer spectra are described by two Lorentzian-shaped doublets belonging to Fe^{3+} in octahedral environment [5]. The parameters of these doublets are listed in table 2, where shifts δ are given relative to NPS.

Table 2. The parameters of the Mössbauer spectrum of the gel containing 27% of iron

	Fe_1^{3+}	Fe_2^{3+}
δ , mm/s	0.187 ± 0.042	0.195 ± 0.045
ΔE , mm/s	0.804 ± 0.081	0.523 ± 0.087
$G/2$, mm/s	0.190 ± 0.020	0.140 ± 0.020
S_{rel}	0.590 ± 0.090	0.410 ± 0.100

The temperature change of the more sensitive Mössbauer parameter for the gel containing 14% of Fe_2O_3 is shown in figure 7.

The shifts change as usual up to 370 K, but at more temperature incline of the temperature dependence get more sharp, that caused by change of the dynamical properties of the structure.

It can be seen from figure 7, the temperature dependencies of quadrupole splitting have peculiarity at 370 K too. Besides, the weak change of the incline of the dependencies is observed at 220 K that is more obvious for Fe^{3+} . This change is connected with the alteration of environment of these ions.

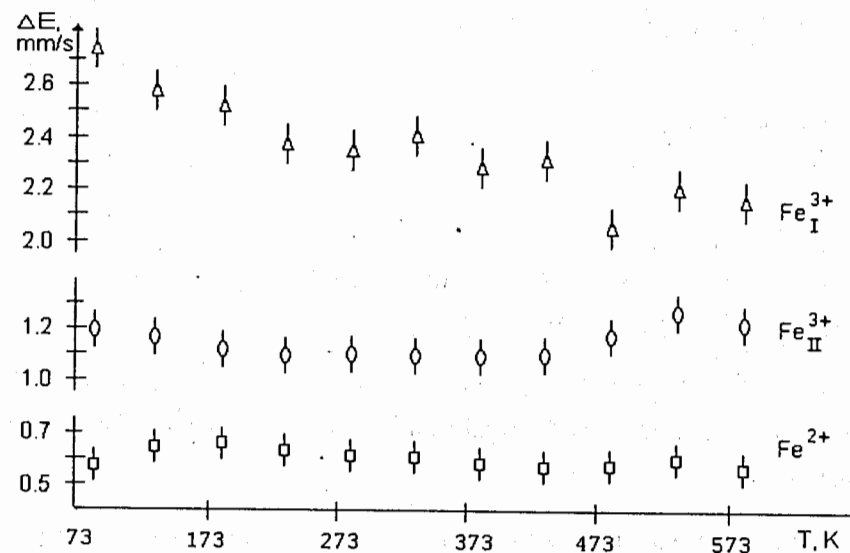


Fig.7. Temperature dependencies of the quadrupole splitting for the gel containing 14% of Fe_2O_3 .

At temperature higher 570 K very strong change of intensity of the doublets is observed because the destruction of initial structure and irreversible phase changes begin. It was very difficult to give quantitative values of the parameters of these phases from their weak intensities.

In gels containing Fe_2O_3 more than 20% the states with two or three non-equivalent Fe^{3+} positions take place.

After annealing samples at 1270 K the magnetic hyperfine structure appears. The field value is about 510 kOe. This fact gives the evidence of appearance of hematite ($\alpha\text{-Fe}_2\text{O}_3$) or hematite with impurities.

The EPR-spectra of these samples consist of two lines at $g=2$ ($\Delta H_1=35$ G, $\Delta H_2=1500$ G). With the increase of Fe_2O_3 content in samples the following narrowing of sharp line and the broadening of wide line takes place. If the Fe_2O_3 content is more than 30% the sharp line disappears.

Taking into account this fact we can confirm that the ferrigel phase within initial gel begins to increase.

Thus, during annealing of gels of the second group it can be observed the formation of ferrigel phase that transforms in hematite at 1270 K.

Data of papers [6,7] show that gels of alumo-ferro-sulphate - phosphate composition have hydroxyl water from 25% to 40%. Since water molecules form various bonds (in length and strength) and they have seven temperature points by which the water structure transformations take place and its properties as solvent change very strong [8], it ought to consider the influence of water hydrogen bonds on crystal structure in the study of mineral formation.

Our investigation allows to confirm, that there are two intervals, in which the essential changes of gels' structure take place: 210...230 K and 380...420 K. The first structure transformation is caused by change of Fe^{3+} environment due to H_3O^+ - groups' mobility in gels. The second interval is connected with destruction of these groups.

In gels containing Fe_2O_3 more than 20% iron has own phase in gel structure. Iron phase can be center of crystallization. Similar results were obtained by Rengesamy [9] and Kishna [10] for amorphous ferri-alumosilicates.

In gels containing Fe_2O_3 more than 30% the ferrigel phase is increasing and after annealing at 1270 K the hematite appears.

More detailed information on the structure of colloids and on the character of phase transformations can be obtained by means of neutron scattering methods on IBR-2 reactor (neutron diffraction, small angle and inelastic scattering).

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Структурные трансформации в природных гелях
по данным резонансных методов исследования

Природные гели алюмо-железо-сульфатно-фосфатного состава исследовались методами мессбауэровской спектроскопии, ЭПР и протонного ЯМР. Анализ температурной зависимости полученных спектров позволил установить два интервала, в которых происходят структурные трансформации в гелях: 213...233 К и 383...423 К. Структурные изменения зависят от содержания железа. С увеличением содержания железа возрастает его роль. В гелях, содержащих более 30% железа, образуются ферригели, которые переходят в гематит после отжига образцов при 1270 К.

Работа выполнена в Лаборатории нейтронной физики им. И.М.Франка ОИЯИ.

Сообщение Объединенного института ядерных исследований. Дубна, 1995

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Structural Transformations in Natural Gels According
to Resonance Methods Data

The natural gels of alumo-ferri-sulphate-phosphate composition were studied by means of the Mössbauer spectroscopy, EPR and NMR'H. The investigation of the temperature dependences of the obtained spectra allowed one to establish two intervals in which the structural transformations of gels take place: 213...233 K and 383...423 K. The structural changes depend on the iron content. With the increase of iron content, its role increases, too. In gels containing iron more than 30%, the ferrigels are formed, which transform to hematite after annealing of samples at 1270 K.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR.

Communication of the Joint Institute for Nuclear Research. Dubna, 1995