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Magnetic properties of $NaNiFe_2(VO_4)_3$ compound at low temperatures

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In the low temperature region, a change in the magnetic state was detected in the new $NaNiFe_2(VO_4)_3$ magnetic compound, confirmed by the results of experimental study by gamma resonance and magnetometry methods. The formation of disordered magnetism in multicomponent vanadate is facilitated by the features of the crystal structure, in which magnetically active cations occupy several crystallographically non-equivalent mixed positions with uneven filling with iron and nickel ions.

Keywords: multicomponent vanadates, magnetic properties, spin disorder.

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1. Introduction

It is known that vanadium is used as a doping element to produce steels for spacecrafts and defense equipment, aircrafts and automotive engineering, nuclear power industry. The actuality of search, synthesis, and studying properties of new vanadium-containing materials is due to the possible extension of their fields of application.

Implantation of transition metal ions to the structure of vanadium-based oxide compounds results in changes in the crystal structure, physical properties, in particular, occurrence of the magnetodielectric effect, as well as formation of magnetoactive cations of subsystems with competing magnetic couplings [1–7]. In this context studying properties of multicomponent vanadates is of interest for the physics of condensed state, chemistry, material engineering.

The $NaNiFe_2(VO_4)_3$ multicomponent vanadate is a new magnetic material synthesized by the method of solid-state reaction [8]. Its physical properties considerably differ from the properties of materials with the chemical formula of $ACuFe_2(VO_4)_3$ $(A = \mathrm{Na, Li})$ [3,4,6]. It follows from the results of X-ray diffraction analysis, that crystal structure of the $NaNiFe_2(VO_4)_3$ nickel-containing vanadate at room temperature is described by the triclinic space group of symmetry $P1$, which is different from P-1 that characterizes compounds with copper, i.e. $LiCuFe_2(VO_4)_3$ and $NaCuFe_2(VO_4)_3$.

The formation of magnetic ordering in the complex oxides based on vanadium, two-valence metals M(II), and three-valence iron of the following system: $A(\mathrm{I})M(\mathrm{II})Fe_2(VO_4)_3$ (A = Li, Na), where magnetoactive cations occupy several crystallographically non-equivalent positions is due to a complex playing of competing exchange couplings with different signs and magnitudes, resulting, as it is shown by experiments, in magnetic properties dependent on the type of both M(II) cations and A(I) cations [3,4,6]. As a result of the experimental studying of magnetism of the $NaNiFe_2(VO_4)_3$ oxide compound with Fe^{3+} and Ni^{2+} magnetoactive cations in a temperature range of $77 < T < 830\,\mathrm{K}$, ferromagnetic behavior of the sample is found along with paramagnetic properties [8], which is indicative of magnetic heterogeneity of the sample. Note, that the multiphase structure (magnetic heterogeneity) of multicomponent compounds with vanadium was noticed in a number of compounds with general formula of $M_3Fe_4V_6O_{24}$ (M = Zn, Cu, Mn, Mg) in the course of studying the competing magnetic couplings by the electron paramagnetic resonance (EPR) method [2,4].

In this work we present the results of studying properties of $NaNiFe_2(VO_4)_3$ polycrystal at low temperatures. In particular, of interest is the evolution of the gamma-resonance spectrum and static magnetic characteristics of the sample with decrease in temperature. The obtained results supplement the information on magnetic properties of the compound containing ions of vanadium and transition metals.

2. Sample synthesis and experimental technique

The $NaNiFe_2(VO_4)_3$ chemical compound is produced through the solid-phase reaction from mixtures of Na_2CO_3, Fe_2O_3, NiO, V_2O_5 powder oxides taken in the stoichiometric ratio at temperatures of 600−640°C. Chemical and phase composition of synthesized samples was controlled by the method of X-ray diffraction analysis on a D8 ADVANCE diffractometer by Bruker using a VANTEC linear detector and CuK_α-radiation. X-ray experiment data and structural characteristics of $NaNiFe_2(VO_4)_3$ are shown in [8].

The Mössbauer spectra of $NaNiFe_2(VO_4)_3$ are measured by a MS-1104Em spectrometer (Research Institute of Physics of the Southern Federal University) in the transmission geometry with a Co^{57}(Rh) radioactive source in the

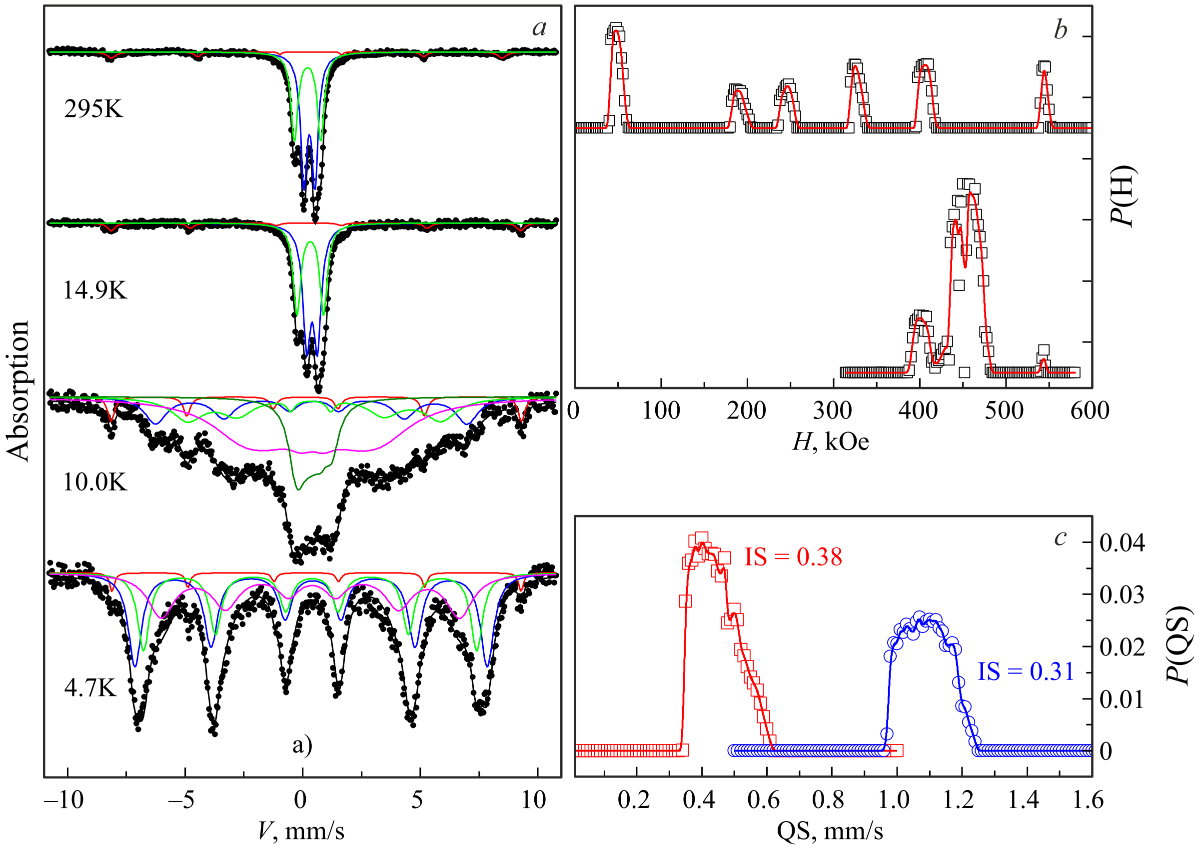

Figure 1. *a* — Mössbauer spectra of NaNiFe$_2$V$_3$O$_{12}$, measured at different temperatures. Color lines show the spectral components, which parameters are presented in the table; *b* — probability distribution of hyperfine fields on iron nuclei in experimental spectra at low temperatures; *c* — probability distribution of quadrupole splittings in the experimental spectrum measured at room temperature.

Mösbauer parameters ^{57}Fe in NaNiFe$_2$V$_3$O$_{12}$

	IS, mm/s ± 0.02	H, kOe ± 5	QS, mm/s ± 0.04	W_{34-16}, mm/s 0.04	A, fr.% ± 0.03	Phase
4.7 K	0.51	467	−0.16	0.68	0.37	NaNiFe$_2$V$_3$O$_{12}$
	0.46	441	−0.16	0.60	0.27	
	0.47	395	−0.14	1.10	0.33	
	0.48	542	0.87	0.25	0.03	α-Fe$_2$O$_3$
10 K	0.53	413	−0.24	0.83−1.12	0.15	NaNiFe$_2$V$_3$O$_{12}$
	0.52	335	0.31	0.42−1.64	0.17	
	0.51	184	−0.04	1.34−3.31	0.46	
	0.49	49	0.28	0.74	0.17	
	0.46	544	0.91	0.36	0.05	α-Fe$_2$O$_3$
14.9 K	0.51	–	0.45	0.40	0.53	NaNiFe$_2$V$_3$O$_{12}$
	0.43	–	1.13	0.38	0.40	
	0.52	542	0.61	0.40	0.07	α-Fe$_2$O$_3$
295 K	0.39	–	0.47	0.33	0.54	Fe^{3+}(6), Fe^{3+}(5) in NaNiFe$_2$V$_3$O$_{12}$
	0.32	–	1.12	0.35	0.40	
	0.37	516	−0.34	0.15−0.44	0.06	Fe^{3+}(6) in α-Fe$_2$O$_3$

Note. IS — isomer chemical shift in relation to α-Fe, H — hyperfine field on the iron nucleus, QS — quadrupole splitting, W — width of internal 34 and external 16 lines of the sextet, A — area under the partial spectrum (fractional population of non-equivalent positions of iron).

temperature range of 4–300 K using a CFSG-311-MESS cryostat with a sample in the form of powder with a thickness of 5–10 mg/cm^2 by natural content of iron in the exchange gas („Cryotrade" LLC).

Static magnetic characteristics of samples are measured on a SQUID-magnetometer of original design by the Kirensky Institute of Physics of the Federal Research Center KSC of the SB RAS [9] in a temperature interval of 4–300 in two modes: field-cooled (FC) and zero-field-cooled (ZFC) sample.

To measure the temperature dependence of dielectric permittivity α, samples were produced in the form of plate with epoxy adhesive with silver filler applied on the opposite planes. Electric capacitance of the obtained capacitor was measured using an Agilent E4980A instrument.

3. Experimental results and discussion thereof

3.1. Results of Mössbauer spectroscopy

To determine the state of iron in the NaNiFe$_2$(VO$_4$)$_3$ sample, the Mössbauer spectroscopy investigation was carried out. Fig. 1, *a* shows spectra at temperatures $T = 295$, 14.9, 10, 4.7 K. The spectra were processed in two steps. At the first step probability distributions of hyperfine fields $P(H)$ (Fig. 1, *b*) and quadrupole splittings $P(QS)$ were determined in the experimental spectra (Fig. 1, *c*). At the second step, based on the information obtained from the $P(H)$ and $P(QS)$ distributions, model spectra were plotted, which were fitted to the experimental spectra by varying all the hyperfine parameters using the least square method in a linear approximation. The Mössbauer spectra were modelled by Lorentz lines taking into account the broadenings caused by magnetic and crystallographic heterogeneity of samples. Parameters of gamma-resonance spectra of the sample under study are shown in the table.

Mössbauer spectrum at a temperature of 295 K is a sum of quadrupole doublets and a Zeeman sextet with low intensity (Fig. 1, *a*). The main part of the sample under study (~ 95 at.%) is the NaNiFe$_2$V$_3$O$_{12}$ oxide compound. Mössbauer parameters of sextet coincide with parameters of the α-Fe$_2$O$_3$ hematite, that is contained in the sample in an amount of 5 ± 2 at.% Fe, table.

The Mössbauer spectrum at room temperature, which is a sum of quadrupole doublets, is typical for the paramagnetic state of the NaNiFe$_2$V$_3$O$_{12}$ magnetic system.

It follows from the analysis of the probability distribution of quadrupole splittings in the Mössbauer spectrum (Fig. 1, *c*) taking into account the X-ray data [8], that there are two types of iron atom positions in high-spin state $S = 5/2$ in the NaNiFe$_2$V$_3$O$_{12}$, which are different in their oxygen environment and have different chemical shifts and quadrupole splittings. The positions of iron cations in the octahedral oxygen environment have Mössbauer parameters $IS = 0.39$ mm/s and $QS = 0.47$ mm/s), and in the oxygen environment in the form of square pyramids are characterized by $IS = 0.32$ mm/s and $QS = 1.12$ mm/s) (table).

In the context of our investigation, we see it important that the Mössbauer spectrum of NaNiFe$_2$(VO$_4$)$_3$ measured at different temperatures not only shows a change in Mössbauer parameters, but is substantially changed itself, Fig. 1, *a*. With the sample cooled below 14 K, Zeeman sextets with a high intensity occur in the spectrum, and doublets disappear. Such a change in the spectrum is typical for the transition of the NaNiFe$_2$(VO$_4$)$_3$ magnetic subsystem at a temperature of $T \approx 10$ K from a paramagnetic state to a magnetic-ordered state or to a state of spin glass.

Note, that in an assumption of equal probability of the Mössbauer effect for different positions, the relative quantities of nuclei in different crystallographic positions can be inferred by the intensity of Mössbauer spectral lines. The multiplicity of sextets in the region of low temperatures, the broadening of lines reflect the presence of non-equivalent positions of iron, which are different in the force and nature of magnetic couplings with the nearest magnetoactive cations. In addition, the absence of Gaussian shape of $P(QS)$ distributions (Fig. 1, *c*) is indicative of unequal probability of population of the octahedral and prismatical positions by iron cations and, respectively, nickel cations (table), which is indicative of an additional disordering in the magnetic subsystem of the sample.

3.2. Dielectric permittivity

The behavior of dielectric permittivity with a change in temperature is studied. Measurement results are shown in Fig. 2.

As can be seen from the figure, the dielectric permittivity increases with increase in temperature. In the region of temperatures of $T = 10$–12 K there is no anomaly on the dependence of dielectric permittivity on temperature, which is typical for the phase transition to a magnetic-ordered state.

3.3. Static magnetization

Results of investigation of static magnetic properties of NaNiFe$_2$(VO$_4$)$_3$ in the region of low temperatures are shown in Fig. 3. Temperature dependencies of magnetization $\sigma(T)$ are measured in modes of magnetic field-cooled (FC) sample (mass $m = 0.125$ g) and zero-field-cooled (ZFC) sample for different values of the external magnetic field ($H = 10$, 25 and 100 Oe). It follows from Fig. 3, that curves are dependent not only on temperature, but also on the magnetic history of the sample. Curves of dependencies of magnetization $\sigma(T)$ measured in FC and ZFC modes show a divergence with decrease in temperature. These features for low external magnetic field can be related to the presence of spin disordering resulting in a magnetic state, which is typical for spin or cluster spin glasses [10]. Note that spin disordering was observed

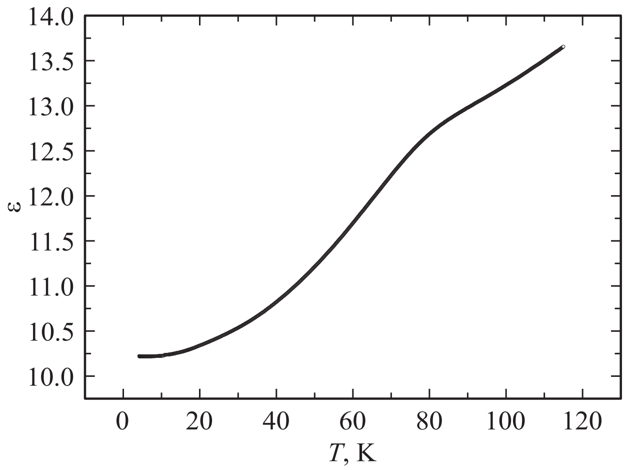

Figure 2. Temperature dependence of dielectric permittivity ε measured at a frequency of 100 kHz in $NaNiFe_2(VO_4)_3$.

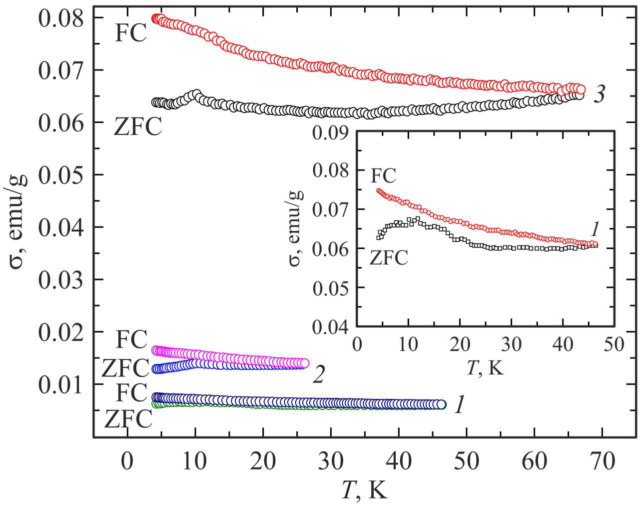

Figure 3. Temperature dependencies of $NaNiFe_2(VO_4)_3$ magnetization measured in modes of magnetic field-cooled (*FC*) sample and in zero-field-cooled (*ZFC*) sample at three different values of the external magnetic field $H = 10$ Oe (curves *1*), 25 Oe (curves *2*), and 100 Oe (curves *3*). The insert shows magnetization as a function of temperature for $H = 10$ Oe.

before in the $NaCuFe_2(VO_4)_3$ vanadate at a temperature below 6 K [6,7].

According to the results of X-ray measurements [8], the crystal structure of $NaNiFe_2(VO_4)_3$ contain six crystallographically non-equivalent cation positions. They are occupied by aliovalent and unevenly distributed magnetoactive cations of transition metals of iron Fe^{3+} and nickel Ni^{2+}. Vanadium cations in this compound are present in a non-magnetic V^{5+}-state. Thus, features of the crystal structure promote formation of spin disordering in the magnetic subsystem of the compound under study with exchange couplings having different magnitudes and directions.

As it is shown by the experimental results, temperature of divergence of $\sigma(T)$ curves measured in *FC* and *ZFC* modes is also dependent on the magnitude of the applied magnetic field (Fig. 3). With increase in magnetic field it shifts to the right, considerably exceeding the temperature of 10 K at $H = 100$ Oe, which is typical for low magnetic fields. Properties like these, i.e. the divergence of magnetization temperature dependence curves measured in modes of magnetic field-cooled sample and zero-field-cooled sample were observed in the course of the investigation in weak magnetic fields for many ferromagnetic materials (in both bulk materials and films) and were considered as related to the displacement of walls of magnetic domains [11–13]. Taking into account ferromagnetic properties of the material under study [8], the effect of magnetic walls and domains impact, probably, has been manifested on the temperature dependencies of magnetization of the $NaNiFe_2(VO_4)_3$ compound with change in magnitude of the external magnetic field.

4. Conclusion

Based on the results of investigation of the $NaNiFe_2(VO_4)_3$ compound by methods of Mössbauer spectroscopy, SQUID-metering, measurement of temperature dependence of dielectric permittivity in the region of low temperatures the following is shown.

With decrease in temperature T at $T \sim 10$ K a change in Mössbauer spectrum is observed that corresponds to the transformation of magnetic subsystem of the sample.

Static magnetization of $NaNiFe_2(VO_4)_3$ in the region of low temperatures dependent on the magnetic history of the sample is indicative of the paramagnetic–disordered magnetic state transition with a freezing temperature of $T_f \approx 10$ K, which formation promotes the feature of the crystal structure.

The temperature dependence of dielectric permittivity does not show anomaly in the region of $T \sim 10$ K, that confirms the transition of the spin system to a spin-glass magnetic state.

Conflict of interest

The authors declare that they have no conflict of interest.

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