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Study of Magnetic Properties of Two Samples from $FeVO_4$–$Co_3V_2O_8$ System*

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Two samples containing phases formed in the $FeVO_4$–$Co_3V_2O_8$ system were prepared by a conventional sintering method. The sample designated as H5 was one-phase with the howardevansite-type structure, while the sample designated as HL7 contained a mixture of H-type and lyonsite-type structures. The temperature dependence of the electron paramagnetic resonance (EPR) spectra and static magnetic susceptibility χ was investigated in the temperature range from liquid helium to room temperature. Both the EPR spectra and the dc magnetic susceptibility showed anomalous behavior indicating that the magnetic competition process may be responsible. A comparison of the obtained results with previous studies on related compounds with the same structure, i.e. $M_3Fe_4V_6O_{24}$ (M = Mg(II), Zn(II), and Cu(II)) revealed that the observed anomaly shifted to lower temperatures on replacing the non-magnetic ions by magnetic Co(II) ions. The temperature dependence of the inverse susceptibility χ^{-1} indicates the existence of antiferromagnetic interactions between Fe(III) and Co(II) spins in sample H5. The obtained values of the Curie-Weiss temperatures are lower than for the $Mn_3Fe_4V_6O_{24}$ compound and comparable to compounds from $M_3Fe_4V_6O_{24}$ systems with M diamagnetic cations. The introduction of cobalt cations intensifies the magnetic frustration what is reflected in the temperature dependence of the magnetic susceptibility at low temperatures.

Keywords: *magnetic properties; electron paramagnetic resonance*

1. Introduction

Multicomponent vanadates forming in the $FeVO_4$–$Co_3V_2O_8$ system have been prepared recently [1, 2]. The phase composition of these samples consists of two different phases: one is of the howardevansite type structure (H-type phase) and the other is of the lyonsite type structure (L-type structure). The composition of the H-type phase corresponds to the $Co_{2.616}Fe_{4.256}V_6O_{24}$ formula [1]. The H-type structure is characterized by the existence of an edge sharing octahedral dimers of iron, connected by VO_4 tetrahedra and two kinds of copper polyhedra: square planes and trigonal bipyramids. Some cationic disorder between octaheral iron and fivefold coordinated copper sites was detected by Mossbauer spectroscopy. This composition differs from the composition of other phases by the howardevansite type structure (with one diamagnetic ion in the cation position) studied by our group previously, i.e. $M_3Fe_4V_6O_{24}$ (M = Mg and Zn) [3–5]. The L-type phase forming in the $FeVO_4$–$Co_3V_2O_8$ system has a homogeneity range with the formula $Co_{3+1.5x}Fe_{4-x}V_6O_{24}$ (where $0.476 < x < 1.667$) [1].

The electron paramagnetic resonance (EPR) measurements at room temperature of 20 different samples formed in the $FeVO_4$–$Co_3V_2O_8$ system showed the presence of three types of magnetic centers [2]. Strong EPR signals were attributed to Fe(III) ions in the $FeVO_4$ phase, while much

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weaker signals – to Fe(III) ions placed in the H-type phase. The third type of the detected signals was due to the ferromagnetic resonance (FMR) lines attributed to iron and/or cobalt residing in clusters of very small sizes in the L-type phase and in the $Co_3V_2O_8$ compound.

As multicomponent vanadates forming in the $FeVO_4$–$Co_3V_2O_8$ system as well as similar $M_2FeV_3O_{11}$ and $M_3Fe_4V_6O_{24}$ compounds possess very interesting physical properties and can be interesting from the point of view of catalysis, the detailed knowledge of their magnetic properties is crucial [3–18]. A strong antiferromagnetic interaction with a very high Curie-Weiss temperature of about T = 200 K was detected for $M_3Fe_4V_6O_{24}$ compounds in the high temperatures range. Competition of different magnetic interactions leads to the observed frustration phenomena at low temperature [17–20]. Replacement of non-magnetic cations with magnetic ions causes an essential increase in the Curie-Weiss temperature [16]. Lowering of the crystallographic symmetry in $M_2FeV_3O_{11}$ as compared to the $M_3Fe_4V_6O_{24}$ system and replacement of smaller cations with bigger ions could also significantly reduce the Curie-Weiss temperature and cause the frustration phenomena to appear in the low temperature range [21].

The aim of this work is to study the magnetic properties of two samples containing multicomponent vanadates formed in the $FeVO_4$–$Co_3V_2O_8$ system in different temperature regions by dc magnetic susceptibility and EPR methods. One of the samples is a monophase containing only a single phase with the howardevansite type structure (H-type phase) and corresponds to the $Co_{2.616}Fe_{4.256}V_6O_{24}$ formula. As in [1] this sample was designated as Sample No. 5, in this paper, we have designated it as H5. The second sample is a mixture of H-type and L-type phases and in [1] it was designated as No. 7. In this paper this sample will be designated as HL7.

2. Experimental

Two samples containing phases formed in the $FeVO_4$–$Co_3V_2O_8$ system were prepared by a conventional sintering method according to the procedure described in [1]. Two mixtures of the following compositions were prepared: 81 mol% $FeVO_4$ and 19 mol% $Co_3V_2O_8$ (the sample designated as HL7) as well as 83 mol% $FeVO_4$ and 17 mol% $Co_3V_2O_8$ (sample H5). The initial mixtures, having been homogenized by grinding, were heated in air for several stages until the composition of the samples did not change after two consecutive heating stages. The heating stages were as follows: 680 °C (20 h) + 780 °C (20 h) + 840 °C (20 h) × 2. After each heating stage, the samples were gradually cooled down in a furnace to room temperature, ground and examined by the XRD method with respect to their composition. The identification of the phases was conducted on the basis of the data presented in work [22].

The dc susceptibility measurements were carried out using an MPMS-5 SQUID magnetometer in the temperature range of 2 – 300 K and magnetic fields up to 50 kOe in the zero-field-cooled (ZFC) and field-cooled (FC) modes.

The EPR/FMR spectra were recorded using a standard X-band Bruker E 500 spectrometer ($\nu = 9.45$ GHz) with magnetic field modulation of 100 kHz. The magnetic field was scaled with an NMR magnetometer. The measurements were performed in the 3 – 290 K temperature range using an Oxford helium-flow cryostat.

3. Experimental results and discussion

3.1. XRD measurements

The starting vanadates react with each other and the phases with the lyonsite (L-type phase) and howardevansite (H-type phase) type structure are formed. Fig. 1 presents the XRD patterns of both the samples after the last heating stage. Sample H5 is a monophase and it contains only the H-type phase with the formula $Co_{2.616}Fe_{4.256}V_6O_{24}$. Sample HL7 is a mixture of two phases: besides the H-type phase it contains a small amount of the L-type phase.

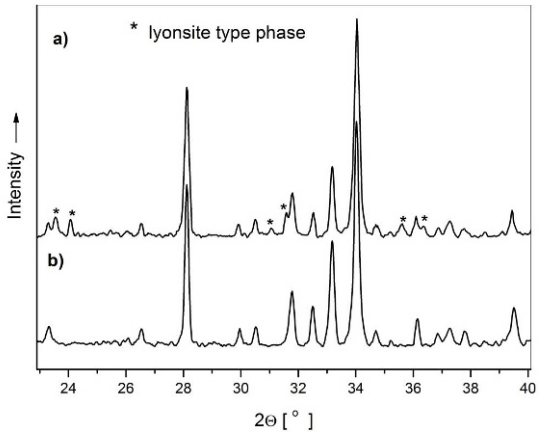


Fig. 1. XRD patterns of two samples of the $FeVO_4$–$Co_3V_2O_8$ system, (a) sample HL7 and (b) sample H5.

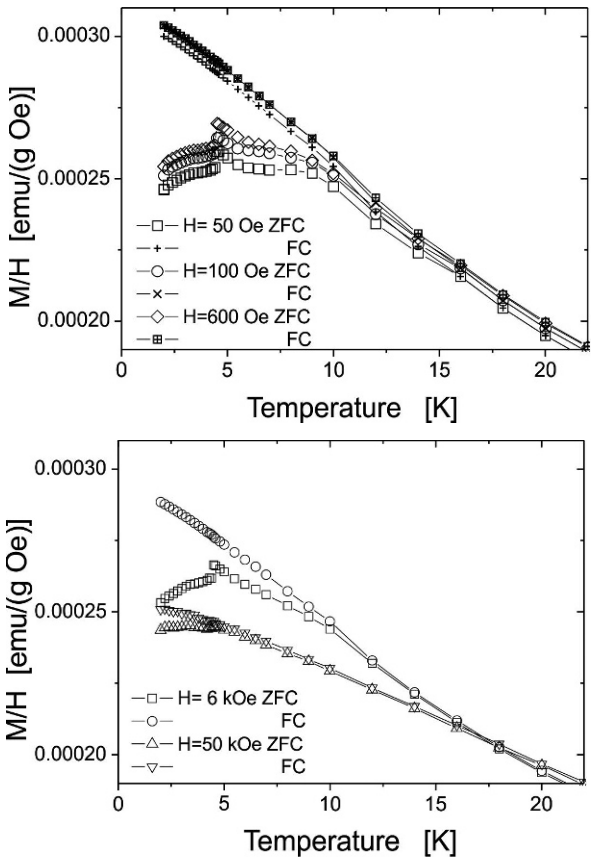


Fig. 2. Temperature dependence of dc magnetic susceptibility in ZFC and FC modes for sample HL7 at low temperatures taken at different external fields. The upper panel shows dependence χ(T) registered at H = 50, 100 and 600 Oe, while the lower panel, at H = 6 and 50 kOe.

3.2. DC magnetic measurements

The results of the dc magnetization studies of both samples are presented in Figs. 2, 3, 4, 5, 6. Figs. 2 and 3 present the temperature dependence of the magnetic susceptibility χ(T) and χ^{-1}(T) in FC and ZFC modes for different values of the applied magnetic field for sample H5. Figs. 4, 5, 6 show similar dependences for sample HL7. The temperature dependence of magnetic susceptibility shows the Curie-Weiss-type behavior for both samples. The Curie-Weiss fit to $\chi^{-1}(T)$ and the obtained values of Curie-Weiss temperatures and effective magnetic moments at different applied magnetic fields are presented in Table 1. The antiferromagnetic interaction (AFM) is dominating as indicated by the negative sign in both samples. The Curie-Weiss temperature is higher than for samples $M_3Fe_4V_6O_{24}$ (M(II) = Cu(II), Zn(II) and Mg(II)) and essentially lower than for the sample with M(II) = Mn(II)) [15, 16, 21]. The magnetic field dependence of this temperature for sample HL7 is similar as for the $Mn_3Fe_4V_6O_{24}$ compound with a maximum for applied field of 6 kOe while the maximum for other $M_3Fe_4V_6O_{24}$ compounds was observed at 50 Oe [23]. Substitution of additional magnetic ions has an essential effect on the reorientation processes of the spin system by the applied external magnetic field. Replacement of non-magnetic cations by strong magnetic ions (Mn(II) and Co(II)) has a strong influence on the magnetic interactions in the system with manganese ions. The values of effective magnetic moments in compounds with M(II) = Cu(II), Zn(II) and Mg(II) are $\mu_{eff} < 12\ \mu_B$ what is smaller than those obtained in this work and are similar as for the $Mn_3Fe_4V_6O_{24}$ compound. Sample H5 did not show the influence of an external magnetic field on both parameters. The greater value of μ_{eff} for sample H5 and a smaller value of the Curie-Weiss temperature indicates the existence of a more complicated magnetic state in sample HL7. Smaller values of μ_{eff} at higher applied magnetic fields could be connected with the fact that some fraction of the correlated spin system could undergo spin-flop transitions. The low magnetization at low temperature, sustained up to 50 kOe, confirms the

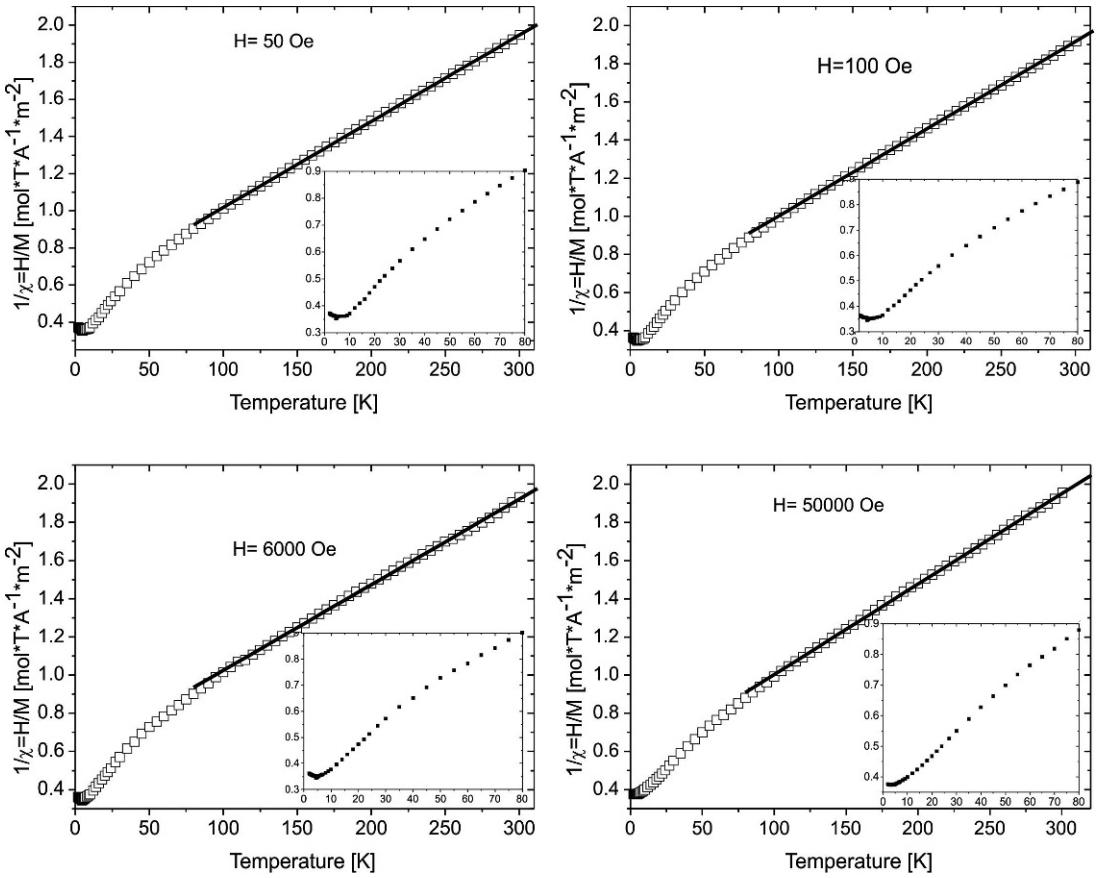


Fig. 3. Temperature dependence of the inverse of dc magnetic susceptibility in ZFC and FC modes for sample HL7. Four panels show dependence χ^{-1}(T) registered at H = 50, 100, 6000 and 50000 Oe.

strong AFM coupling and the concurrent compensation of some fraction of isolated trivalent iron ions in the high spin $^6S_{5/2}$ ground state and divalent cobalt ions. The ferromagnetic (FM) coupling is observed between 15 K and 70 K with the Curie-Weiss temperature $\Theta = 5(1)$ K which transforms to $\Theta = -10(1)$ K at the high applied field for sample HL7. The FM coupling in this region is $\Theta = 9(1)$ K even in high applied magnetic fields for sample H5.

The low temperature downturn of χ^{-1}(T)) occurs in both samples independent of the different crystal structure. This variation is commonly observed in most frustrated antiferromagnets, implying the presence of antiferromagnetically correlated spin clusters and relatively "loose" spins [24, 25]. Figs. 2 and 4 present the low temperature dependence of the ZFC and FC susceptibility for both samples at different magnetic fields. As the temperature decreases, a distinct kink is observed at $T_1 \sim 10$ K for sample HL7 and at $T_1 \sim 17$ K for sample H5 at low magnetic fields, below which the M_{ZFC} and M_{FC} branches start to diverge, indicating the onset of irreversibility. A cusp like peak

Table 1. Values of parameters obtained from the Curie-Weiss fittings to the temperature dependence of dc magnetic susceptibility.

	Sample HL7		Sample H5	
H [Oe]	μ_{eff} [μ_B]	Θ [K]	μ_{eff} [μ_B]	Θ [K]
50	13.12(3)	−119.0(5)		
100	13.23(3)	−119.4(7)		
600			13.55(3)	−114.9(5)
6000	13.36(3)	−128.5(9)	13.53 (3)	−114.7(5)
50000	12.98(3)	−111.4(9)		

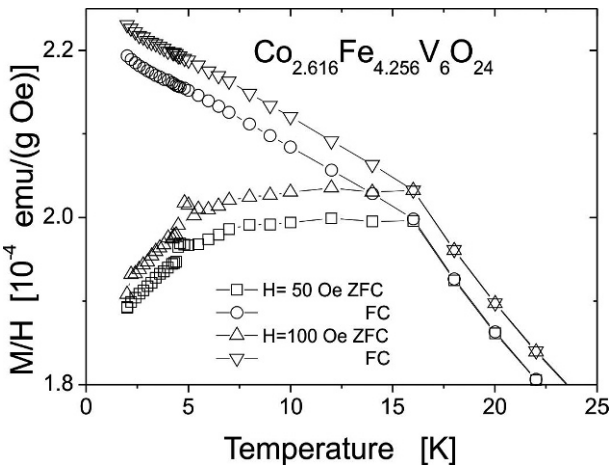


Fig. 4. Temperature dependence of dc magnetic susceptibility in ZFC and FC modes for sample H5 at low temperatures.

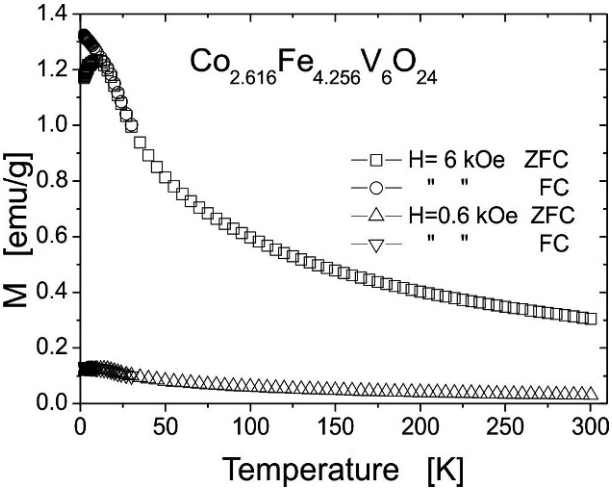


Fig. 5. Temperature dependence of magnetization in ZFC and ZF modes for sample H5.

is successively observed at a lower temperature, $T_2 \sim 5.0$ K, which is similar to the spin-freezing transition previously identified in $M_3Fe_4V_6O_{24}$ (M(II) = Mg(II) and Cu(II)) at $T_f = 3.0$ K [15, 21]. At high magnetic fields ($H = 50$ kOe), both anomalies become smeared out and a flattening of $M/H$is observed below T_2. A comparison between the Curie-Weiss temperatures sets up the mean-field energy scale for the dominant AFM coupling of Fe^{3+} spins and the freezing temperature yields the ratio $f = -\Theta / T_2 \sim 24$ K that shows the presence of significant spin frustration which is lower than

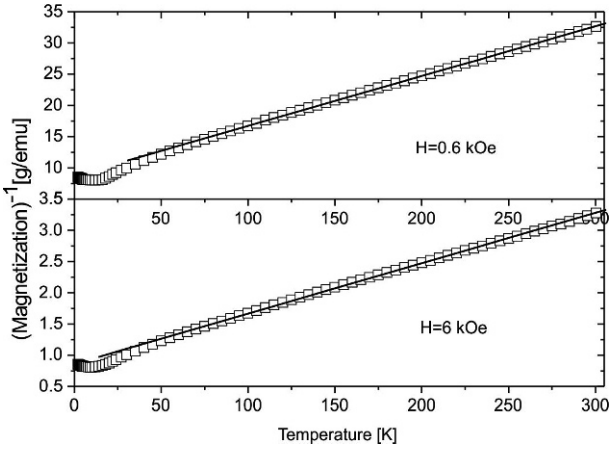


Fig. 6. Temperature dependence of inverse magnetization in ZFC mode at two different magnetic fields for sample H5.

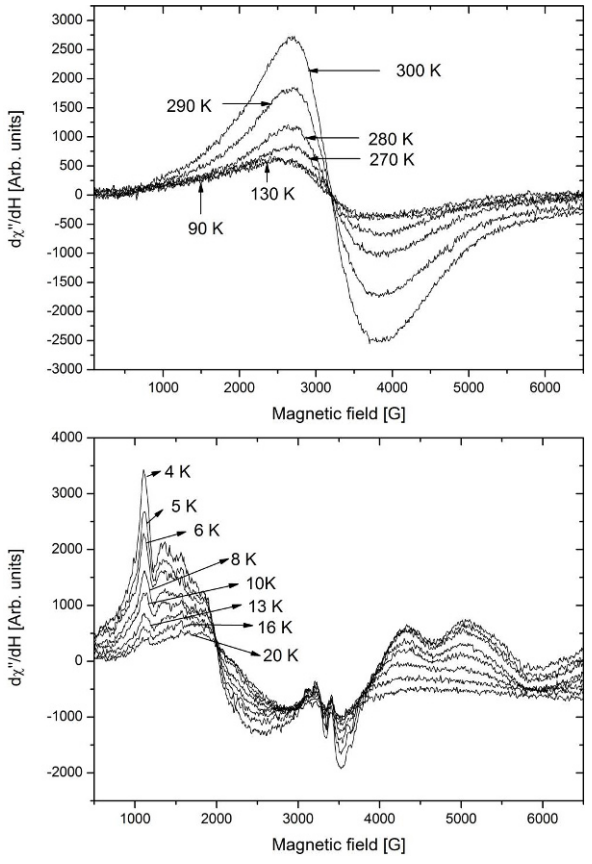


Fig. 7. Magnetic resonance spectra registered at different temperatures for sample HL7. The upper panel shows spectra in the high temperature range, the lower panel, in the low temperature range.

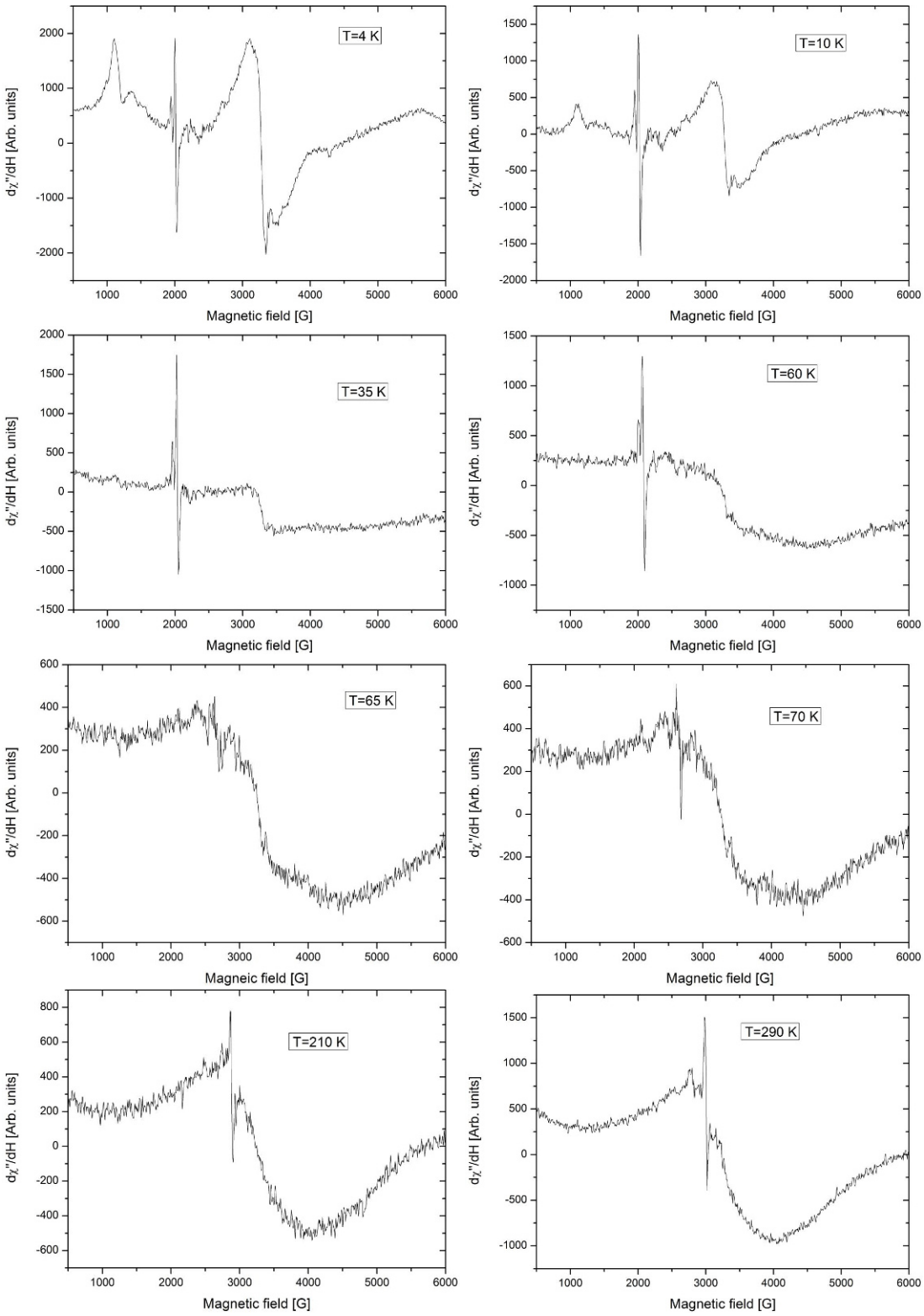
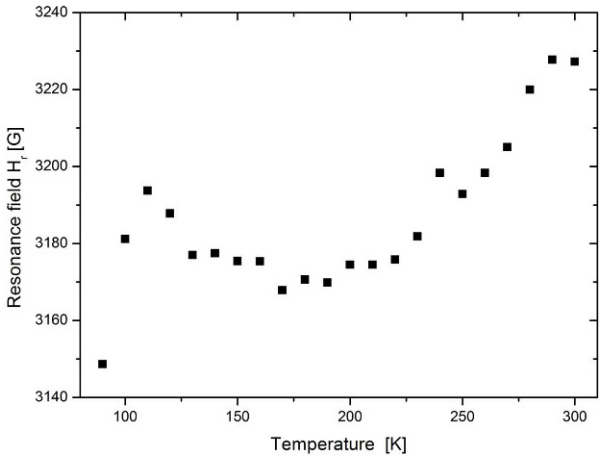
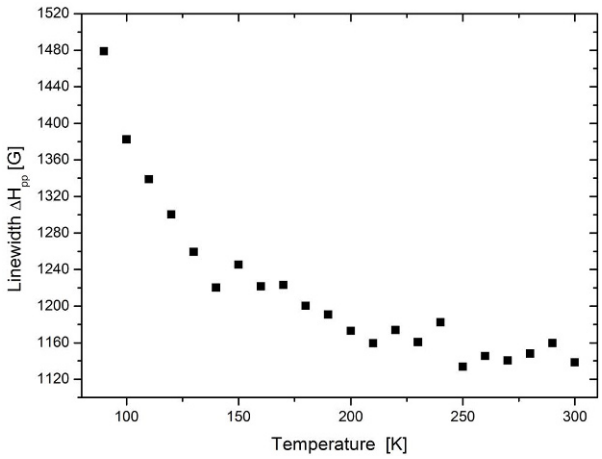


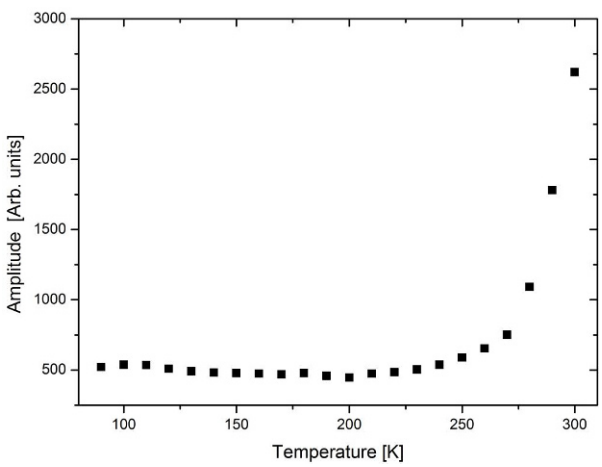
Fig. 8. Magnetic resonance spectra registered at different temperatures for sample H5. Each panel shows the spectrum at specified temperature.



(a)



(b)



(c)

Fig. 9. Temperature dependence of apparent resonance field H_r (a), linewidth ΔH_{pp} (b), amplitude A_{pp} (c) of the resonance signal for sample HL7 calculated by Koksharov's method.

for $Mg_3Fe_4V_6O_{24}$ ($f \sim 37$) and higher than for $Cu_3Fe_4V_6O_{24}$ ($f \sim 19$).

3.3. EPR/FMR measurements

Figs. 7 and 8 present the EPR/FMR X-band spectra registered at different temperatures for HL7 and H5 samples, respectively. In the high temperature range the spectrum is dominated by an asymmetrical, very intense and broad resonance line centered at magnetic field $H_r \sim 3300$ G. EPR spectra from divalent cobalt ions could be observed in the low temperature range. Magnetic resonance spectra at high temperatures for sample HL7 could be analyzed, as a first approximation, by using a procedure appropriate for the FMR spectra resulting from small amounts of magnetic nanoparticles embedded in the non-magnetic matrix, which has been introduced by Koksharov et. al. [26]. This rough approach is very helpful in determining whether a superparamagnetic state of a spin system exists in our sample. Fig. 9 presents the temperature dependence of the obtained apparent resonance field H_r(T), peak-to-peak linewidth ΔH_{pp}(T) and signal amplitude A_{pp}(T) for sample HL7 calculated by this method. The behavior of these parameters suggests that the magnetic resonance spectra are arising from magnetic nanoparticles or nanoclusters of magnetic ions [27].

For a description of the magnetic resonance spectrum of this type a few different relevant lineshapes have been considered [28]. The obtained spectra of sample HL7 have been fitted by two Landau-Lifshitz-shape lines. In case of the linear polarization of the microwave field and for a perfect ferromagnet the following equation for the absorption of the Landau-Lifshitz lineshape could be used [26]:

$$I(H) = \frac{C \cdot H_r^2 \left[\left(H_r^2 + \Delta_H^2\right) H^2 + H_r^4\right] \Delta_H}{\left[H_r^2 (H - H_r)^2 + H^2 \Delta_H^2\right] \left[H_r^2 (H + H_r)^2 + H^2 \Delta_H^2\right]} \quad (1)$$

where C is a numerical constant, H_r is the intrinsic resonance field, and Δ_H is the intrinsic linewidth. The usage of two Landau-Lifshitz-shape lines could be motivated by the existence of magnetic anisotropy in the spin system and random

distribution of magnetic moments of nanoparticles/clusters. These two lines approximate to some degree the parallel and perpendicular components of magnetic moments of nanoparticles in respect to an external magnetic field. Fig. 10 shows, as an example, the observed and fitted spectra of sample HL7 at three selected temperatures. It could be observed that the fitting with two Landau-Lifshitz lines is rather satisfactory.

Fig. 11 shows the temperature dependence of the resonance fields H_r, linewidths Δ_H and amplitudes of resonance signals A_{pp} for the two components (designated as line 1 and line 2) in sample HL7. These parameters were calculated from the fitting of the observed spectra with two Landau-Lifshitz-shape lines. In the high temperature range ($T > 75$ K) the values of these parameters display a week temperature change, but a strong dependence is observed at low temperatures, especially for line 2. Thus, at high temperatures, the magnetic anisotropy is low, but below 75 K, it increases significant with a temperature decrease. Reorientation processes of the collective spin system affect the internal magnetic field and change the resonance condition:

$$h\nu = g\mu_B(H_o H_{int}) \tag{2}$$

where h – Planck constant, ν – resonance frequency, μ_B – Bohr magneton, H_0 – the applied external magnetic field and H_{int} – the internal magnetic field. It can be assumed that at about 75 K there is the so called blocking temperature of the superparamagnetic state of the spin system registered at microwave frequency of the EPR spectrometer.

The magnetic resonance spectrum of sample H5 is much weaker than registered for sample HL7. The integrated intensity I of a magnetic resonance spectrum could be calculated by the formula $I \sim A \cdot \Delta H^2$, where A is the amplitude and ΔH is the linewidth. Assuming that the concentration of spin centers taking part in magnetic resonance is proportional to the integrated intensity, we could estimate that at room temparature $I_{H5}/I_{HL7} \sim 6.5 \cdot 10^{-3}$. Thus, in case of sample H5, we have a very low concentration of magnetic centers. We used the procedure described above [24] to determine the parameters of magnetic resonance spectra of sample H5. Fig. 12 presents the temperature dependence of the FMR parameters (resonance field, amplitude) for sample H5. A narrow magnetic resonance line with an average linewidth of about 35 G is observed from room temperature to 70 K. This

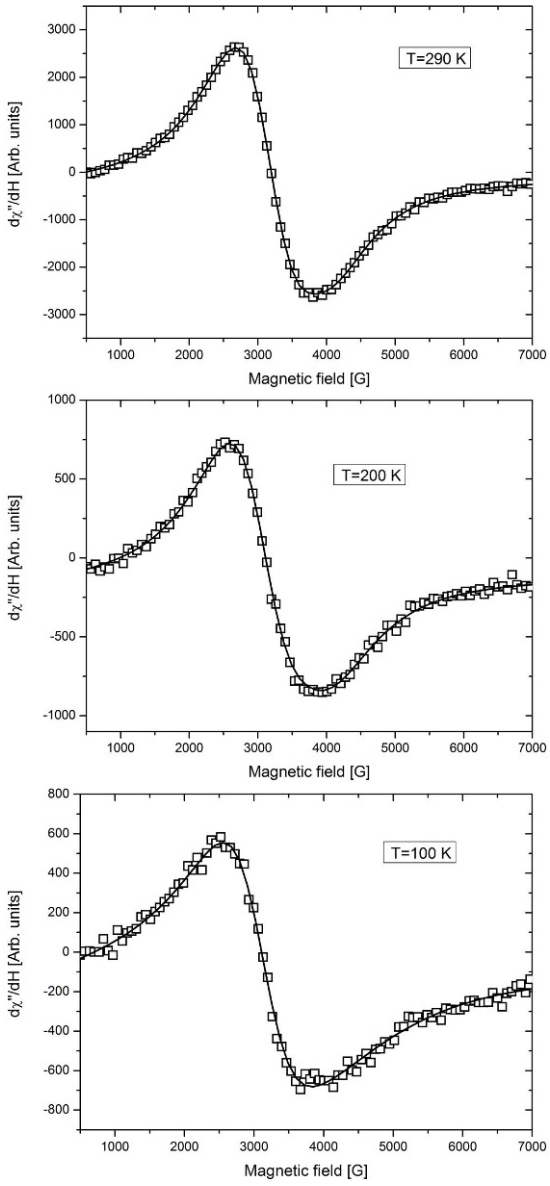


Fig. 10. Fitting of registered FMR spectra (open squares) with the sum of two components of the Landau-Lifshitz – shaped functions (solid line) for sample HL7. The three panels show the fitting at indicated temperatures.

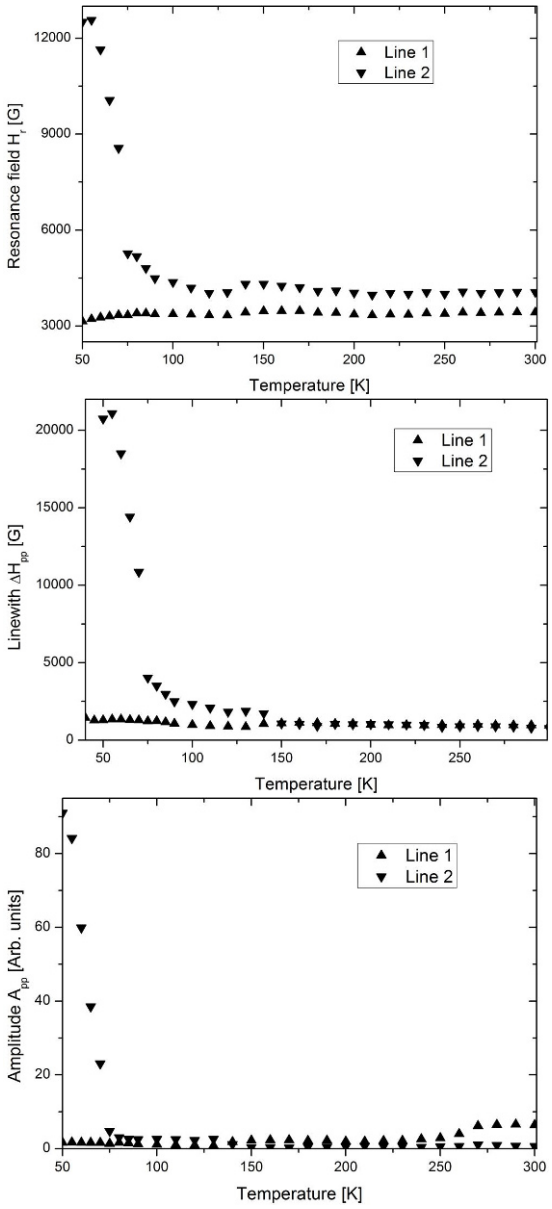


Fig. 11. Temperature dependence of resonance fields H_r (upper panel), linewidths Δ_H (middle panel) and amplitudes of resonance signals A_{pp} (bottom panel) for two components (line 1 and line 2) in sample HL7.

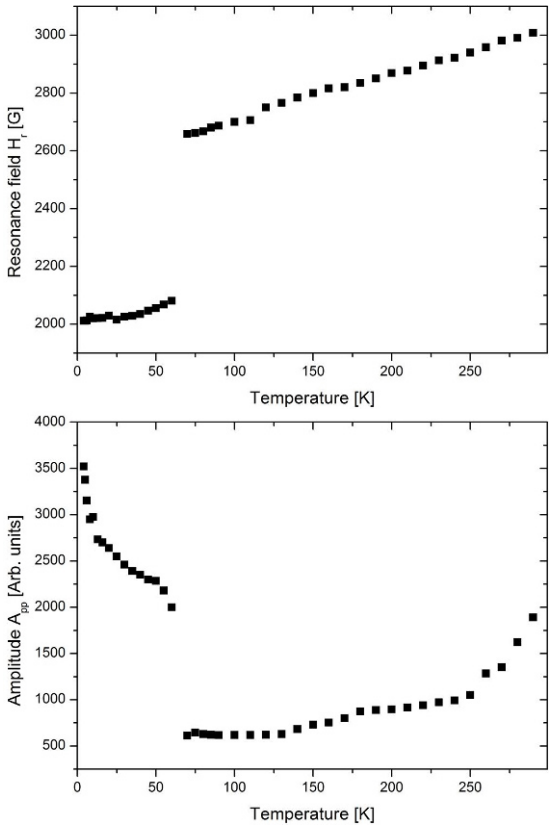


Fig. 12. Temperature dependence of apparent FMR parameters (resonance field, amplitude) for sample H5.

line shifts towards low magnetic fields with a decrease in temperature and disappears unexpectedly at 70 K. It seems to appear again on further cooling of the sample (at about 60 K) but at a much smaller magnetic field. Now, its amplitude increases with a decrease in temperature. This anomalous behavior of the spin nanoclusters in sample H5 seems to be connected with the blocking temperature observed in sample HL7. The unblocking effect seen in sample H5 below 60 K might be also related to a very small concentration of spins in that material.

The EPR spectra of isolated divalent cobalt ions were recorded in both samples (in sample H5 with smaller concentration than in HL7) with the amplitude increasing with a decrease in temperature (see Figs. 7 and 8) [29, 30]. Thus, some of cobalt magnetic ions are not taking part in the ordering processes in the spin system of our samples. The EPR signals for high-spin cobalt(II) are typically observed only below 30 K due to fast spin-lattice relaxation times [27]. The EPR linewidths remain constant in the 4 – 20 K range and the signal intensity grows on cooling the samples. The reciprocal intensity shows the Currie-Weiss behavior with the Curie-Weiss constant (the same for both samples)

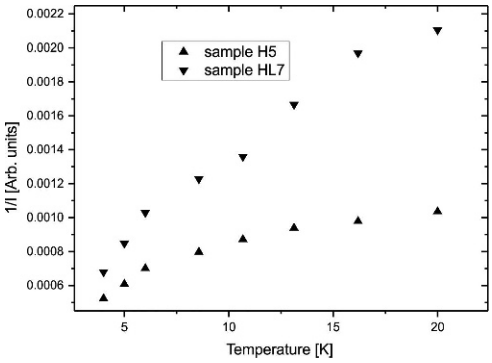


Fig. 13. Temperature dependence of EPR reciprocal intensity due to divalent cobalt ions in both samples.

$\Theta = -2.5$ K (Fig. 13). This negative sign of that constant indicates on the prevailing antiferromagnetic interaction.

4. Conclusions

Two samples from the $FeVO_4$–$Co_3V_2O_8$ system, one containing mixed H-type and L-type phases (sample HL7), and the second with only a single H-type phase structure (sample H5) were synthesized and investigated by magnetic methods. In both samples strong magnetic coupling was observed at high temperatures due to dominating iron ions. Competition processes of iron ions placed in different sublattices prevent creation of a global magnetic ordering at low temperatures as suggested by the Curie-Weiss constant. The observed antiferromagnetic interaction at low temperatures could be due to the divalent cobalt ions. Magnetic frustration phenomena are observed below 5 K. The concentration of magnetic clusters and divalent ions is essentially higher in the sample with mixed phases. The very small concentration of magnetic nanoclusters in sample H5 could be blamed for the anomalous behavior of the magnetic resonance spectra in that sample.

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