



# Competition of Magnetic Interactions in $M_3Fe_4V_6O_{24}$ (M(II)=Zn, Cu, Mn, Mg) Compounds Studied by EPR at High Temperatures



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## Abstract

Multicomponent vanadates  $M_3Fe_4V_6O_{24}$  (M=Zn(II) and Mn(II)) have been synthesized using the solid state reaction method from appropriate  $MO$ ,  $V_2O_5$ ,  $Fe_2O_3$  metal oxides. The temperature dependence of the electron paramagnetic resonance (EPR) spectra has been performed in the 90–290 K temperature range. Both the resonance field and the integrated intensity of the EPR line have shown a minimum at ~230 K. Comparison with a similar study on the  $M_3Fe_4V_6O_{24}$  (M=Mg(II) and Cu(II)) compounds has been made. The observed behaviour of the EPR integrated intensity is similar to what is registered for the nanoscale systems of the exchange coupled magnetic ions. The thermal effect of EPR parameters is more pronounced if two different magnetic ions are present in the same sublattice. The short-range ordered spin clusters interaction and reorientation in the high temperature range could change the effective internal magnetic field which in turn could change the resonance condition and shift the observed resonance line. This behaviour could be attributed to the inherent magnetic inhomogeneity of the system (magnetic multiphase) due to the presence of different valence states of magnetic ions.

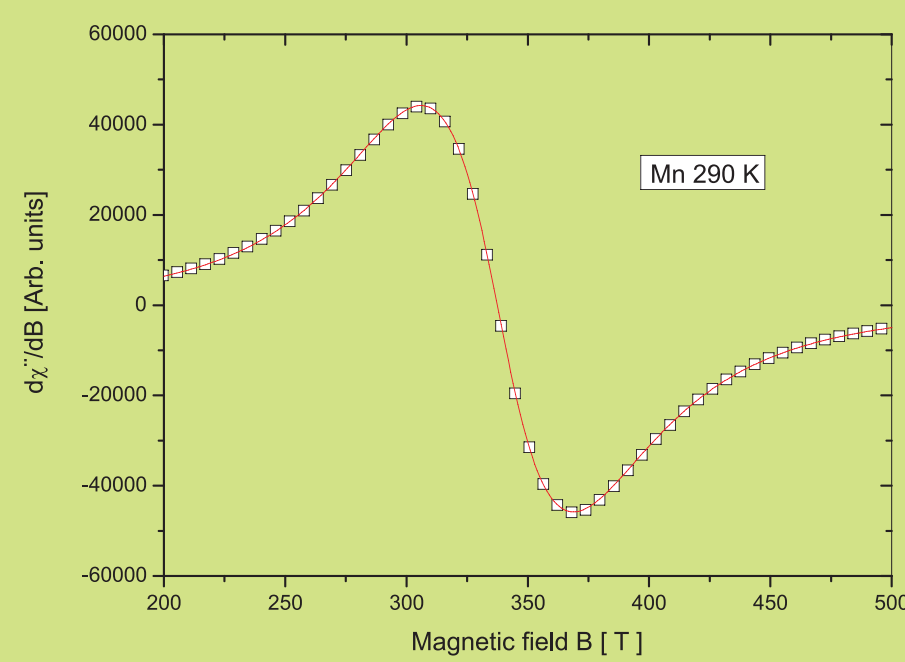


Figure 2. The EPR spectrum of  $Mn_3Fe_4(VO_4)_6$  at 290 K: open squares - experimental points, solid curve - fitting by Lorentzian curve.

## Introduction

The compounds in the multicomponent vanadates systems  $M-Fe(Cr)-V-O$  (M(II)=Zn(II), Mg(II), Ni(II), Cu(II) and Co(II)) are known to display very interesting and complicate physical phenomena. The disorder in position of metal ions and the oxygen deficiency processes could be responsible for the observed frustration effects. Additionally, the coexistence of two different, strong magnetic ions (nickel(II) and iron(III)) could lead to formation of very complicated structural and magnetic states in which the ferroelectric with antiferromagnetic states could be present. In the  $Ni_3FeV_6O_{21}$  compound the temperature dependence of dc magnetic susceptibility has shown some extraordinary behavior at temperatures about 200 K connected with magnetic ordering processes. The temperature dependence of the EPR spectra of  $M_3Fe_4V_6O_{24}$  (M=Zn(II) and Cu(II)) has shown the shift of the resonance line with the minimum value of resonance field at 200 K. In this temperature range the spin system of iron(III) ions is trying to attain an order magnetic state but the competition of magnetic interactions prevents it. In the multicomponent vanadates compounds from the M-In-V-O system with both diamagnetic ions in a single sublattice the vanadium ions complexes in lower oxidation state have been registered. Their presence causes significant complication of the physical state of these compounds. The  $M_3Fe_4V_6O_{24}$  system is providing the opportunity to investigate the role of magnetic inhomogeneity produced by two strong magnetic ions. It will be shown that in the multicomponent vanadates systems two iron(III) ion sublattices compete in formation of long-range ordered states leading to magnetic frustration.

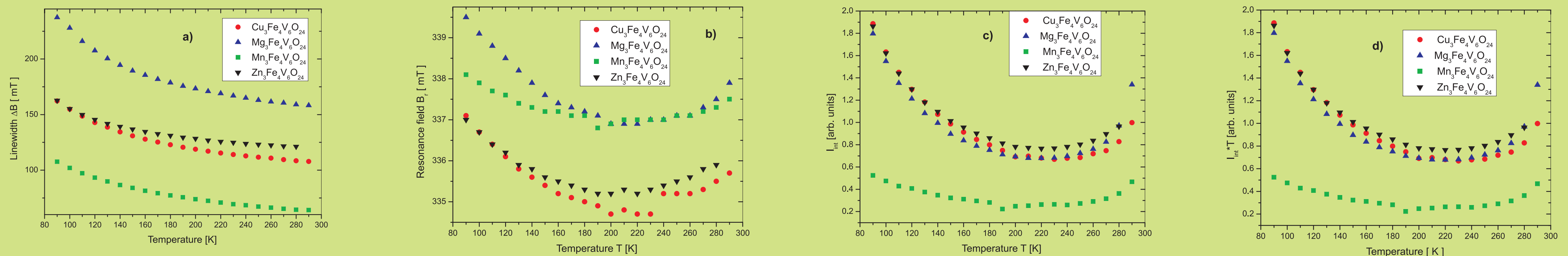


Figure 3 The temperature dependence of the EPR spectral parameters of  $M_3Fe_4(VO_4)_6$  (M(II) =Zn(II), Mg(II), Mn(II) and Cu(II)); (a) the linewidth, (b) the resonance field, (c) the EPR integrated intensity and (d) product of integrated intensity and temperature.

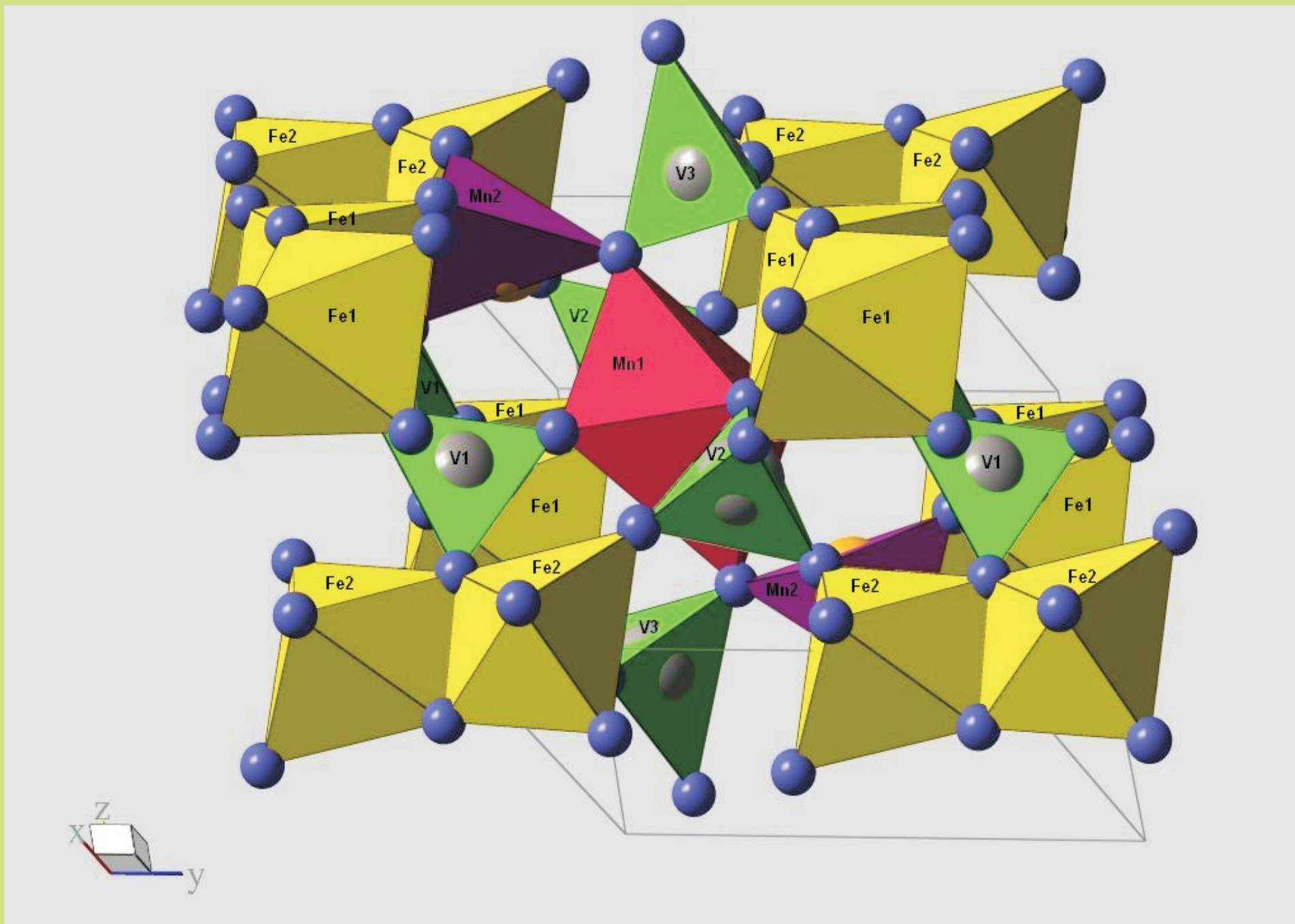


Figure 1. The crystal structure of the  $Mn_3Fe_4(VO_4)_6$  compound with highlighted of metal-oxygen polyhedra.

Table 1 Distances (in nm) between iron(III) ions

Compound	$Mg_3Fe_4V_6O_{24}$	$Cu_3Fe_4V_6O_{24}$	$Zn_3Fe_4V_6O_{24}$	$Mn_3Fe_4V_6O_{24}$
$d_{11} = d_{Fe1-Fe1}$	0.3066	0.3095	0.3117	0.3347
$d_{22} = d_{Fe2-Fe2}$	0.3193	0.3152	0.3192	0.3153
$\Delta d = d_{11} - d_{22}$	-0.0127	-0.0057	-0.0075	0.0194

Table 2 The values of  $\Delta B/\Delta T$  gradient (in mT/K) for two different temperature region

Compound	$Mg_3Fe_4V_6O_{24}$	$Cu_3Fe_4V_6O_{24}$	$Zn_3Fe_4V_6O_{24}$	$Mn_3Fe_4V_6O_{24}$
260-290 K temp. range	0.027	0.017	0.015	0.010
90-150 K temp. range	- 0.032	- 0.030	- 0.023	- 0.015
$T_{minimum}$ [K]	220	230	220	~220

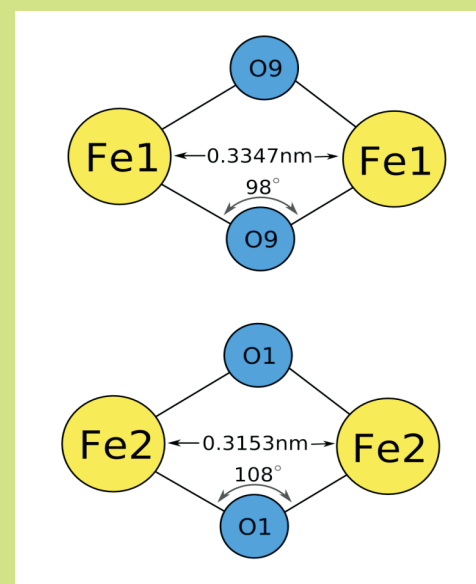


Figure 5. Schematic diagram presenting distances and angles between neighbouring iron (III) ions in Fe1 and Fe2 sublattices in  $Mn_3Fe_4V_6O_{24}$ .

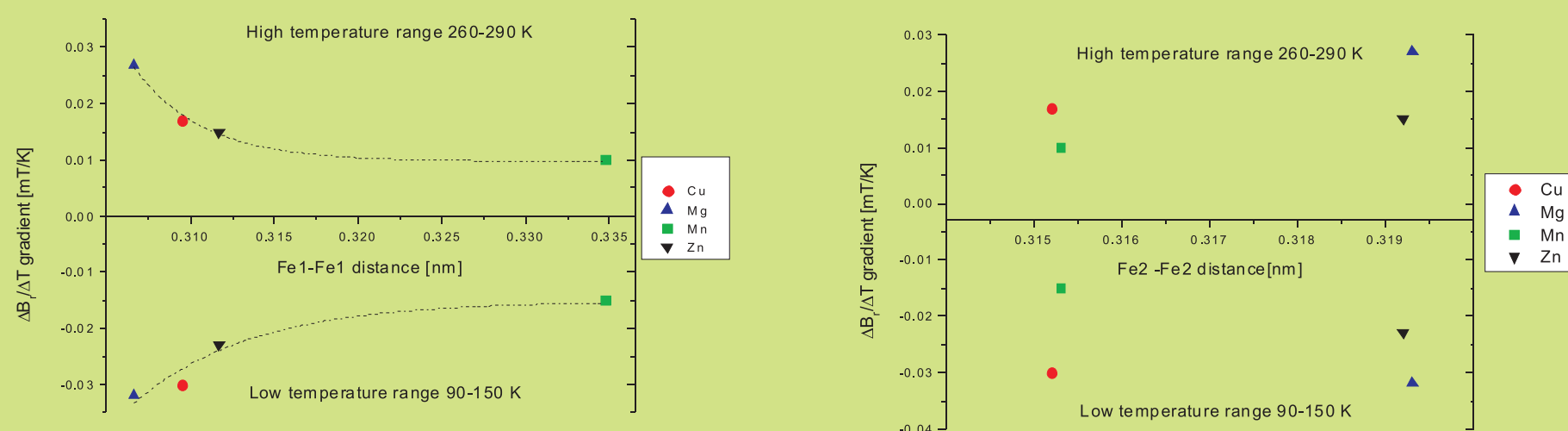


Figure 4. Dependence between the values of the  $\Delta B/\Delta T$  gradients and Fe1-Fe1 distances (a), and Fe2-Fe2 distances (b) for four  $M_3Fe_4(VO_4)_6$  compounds.

## Experimental & Results

Polycrystalline samples of the multicomponent vanadates  $M_3Fe_4(VO_4)_6$  (M=Zn and Mn) were prepared from the solid-state reaction between 37.50 mol.%  $MO$ , 37.50 mol.%  $V_2O_5$  and 25 mol.%  $Fe_2O_3$ . The crystal structure of the  $M_3Fe_4(VO_4)_6$  compound were investigated by the XRD and neutron powder diffraction measurements. The EPR spectra were recorded using standard X-band spectrometer type Bruker E 500 (9.46 GHz) with magnetic field modulation of 100 kHz. The magnetic field was scaled with a NMR magnetometer. The measurements were performed in the temperature range of 90 to 290 K using an Oxford liquid nitrogen flow cryostat and a standard hot air flow system.

$M_3Fe_4(VO_4)_6$  (M=Zn(II), Cu(II), Mg(II) and Mn(II)) system is build up from  $M_1O_6$  polyhedra,  $M_2O_4$  trigonal bipyramids,  $M_3O_6$  and  $M_4O_6$  octahedra and isolated  $VO_4$  tetrahedra. Fe atoms have been found to occupy exclusively the M3 and M4 sites, while M atoms occupies the M1 and M2 ones. Figure 1 shows the  $Mn_3Fe_4(VO_4)_6$  crystal structure, where the Fe dimer network is emphasized, with the Fe2 dimers being those located near the corners of the unit cell. The values of Fe1-Fe1 and Fe2-Fe2 distances are shown in Table 1 for the four different compounds. The distance Fe1-Fe1 is the greatest for the compound with Mn(II) ions and thus the magnetic dipole-dipole interaction could be the weakest for that sample. Figure 3c presents the temperature dependence of the EPR integrated intensity for four diverse compounds differing in type of an ions replacing the M(II) cation position in the system  $M_3Fe_4(VO_4)_6$ . This important spectral parameter is proportional to the magnetic susceptibility of the investigated spin system. For all studied samples the behaviour of the integrated intensity with decreasing temperature is similar and that dependence reaches a minimum at about 220 K. A similar conduct of integrated intensity is observed for the system of magnetic nanoparticles embedded in non-magnetic matrixes. Probably in the  $M_3Fe_4(VO_4)_6$  system nanosize magnetic clusters are formed by magnetic ions placed in different sublattices.

Figure 3b summarizes the temperature dependence of the resonance field for all four samples. Table 2 presents the values of temperature gradient of the resonance field  $\Delta B/\Delta T$  for two regions of temperature. The smallest value of  $\Delta B/\Delta T$  is recorded for sample with Mn(II) ions.

An interesting relationship could be observed between the values of  $\Delta B/\Delta T$  gradients and the distances  $d_{ii}$  for four studied  $M_3Fe_4(VO_4)_6$  compounds (Fig. 4a). The  $\Delta B/\Delta T$  gradients in the 90-150 K range and in the 260-290 K range correlate well with the  $d_{ii}$  distances. A different situation is observed for the Fe2 sublattice. There seems to be no correlation between  $d_{ii}$  distances and the  $\Delta B/\Delta T$  gradients (Fig. 4b). This could indicate on domination in the EPR spectrum of the Fe(III) ions sites in a particular sublattice. There is no apparent correlation between the value of the  $\Delta B/\Delta T$  gradients and the Fe-O-Fe angles between neighbouring iron (III) ions in Fe1 and Fe2 sublattices. The dominating interaction in a specific temperature range could be inferred from the temperature dependence of the product of integrated intensity and temperature that is proportional to the square of an effective magnetic moment (Fig. 3d). Above 180 K the effective magnetic moment decreases with temperature decrease what indicates on domination of the antiferromagnetic interaction. Below 180 K the effective magnetic moment increases with temperature decrease what suggests on domination of ferromagnetic interaction.

The emerging internal magnetic field could provide for modification of the magnetic resonance condition in the following way:

$$h\nu = g\mu_B(B_0 - B_{int}) \quad (1)$$

where  $h$  – Planck constant,  $\mu_B$  – Bohr magneton,  $\nu$  – microwave frequency,  $B_0$  – external applied magnetic field and  $B_{int}$  – internal magnetic field. If it is supposed that the main part of the internal magnetic field arise from the dipole-dipole interactions than the magnetic dipole inside a sample could be subjected to an average magnetic field given by:

$$B_i = \sum [(3\cos^2\theta_i - 1)/r_{ij}^3] \mu_j \quad (2)$$

where  $B_i$  – an internal magnetic field acting on the  $i$ -th magnetic center,  $\theta_i$  – the angle of the  $i$ -th magnetic dipole with the direction of an external magnetic field,  $r_{ij}$  – the distance between magnetic dipoles, and  $\mu_j$  – magnetic moment of the  $j$ -th dipoles. A similar behavior of the resonance field with temperature was observed for magnetic nanoparticles embedded at low concentration in a non-magnetic polymer matrix. The values of the internal magnetic field in that case were strongly dependent on the sizes of magnetic nanoparticle agglomerates. In a system with only one sublattice of Fe(III) ions, e.g. in  $Fe_3VO_8$ , below 200 K an ordered magnetic state was created and the observed resonance field shifted to lower values with the temperature decrease down to very low temperatures. From eq. (2) it is seen that when the value of the geometrical factor fulfils the condition  $\cos^2\theta > 1/3$  the internal magnetic field is positive while for  $\cos^2\theta < 1/3$  it is negative. If the angle  $\theta$  for a part of the spin system fulfils the former condition and the other part the later the shift of resonance field would have an opposite direction. That could explain the thermal behavior of the resonance line, especially for a system with different magnetic sublattices. This would also account for the competition processes that play a very important role in the frustration phenomena. The competition of magnetic interactions is probably responsible for the lack of magnetically ordering states in the  $M_3Fe_4(VO_4)_6$  compounds. The linear change of the resonance field with temperature could be explained by the influences of temperature on the magnetic moment of the cluster (agglomerates) as a result of change of the spin-orbit interaction.

## Conclusion

Coexistence of two subsystems of magnetic iron(III) ions in the multicomponent vanadates compounds  $M-Fe-V-O$  (M(II)=Zn(II), Mg(II), Cu(II) and Mn(II)) has lead to competition of magnetic interactions forming a frustrated system that prevented creation of an magnetic ordered state at high temperatures. Additional magnetic ions in  $M_3Fe_4(VO_4)_6$  (M=Cu and Mn) compounds have formed an extra magnetic sublattice which has a strongly influence on the above ordering processes.

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