COMPETITION OF MAGNETIC INTERACTIONS IN Cu$_3$Fe$_4$V$_6$O$_{24}$ STUDIED BY EPR

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Abstract. Multicomponent vanadate Cu$_3$Fe$_4$V$_6$O$_{24}$ has been synthesised using the solid state reaction method and studied by electron paramagnetic resonance (EPR). Temperature dependence of the EPR spectra has been performed in the 90–290K temperature range. Both the resonance field and the integrated intensity of the EPR line have shown a minimum values at ~230K. This behaviour could be correlated with the reorientation effect of magnetic interactions at higher temperatures, leading to a change of an effective internal magnetic field. Comparison is made between the values of the obtained EPR parameters for the Zn$_3$Fe$_4$V$_6$O$_{24}$ and Cu$_3$Fe$_4$V$_6$O$_{24}$ compounds. The observed effect could be attributed to an inherent magnetic inhomogeneity of the system due to the presence of different magnetic sublattices.

1. INTRODUCTION

Compounds belonging to the multicomponent vanadate Me-Fe-V-O system (Me is metal 3d ion) are very interesting materials suitable for study of their intricate magnetic interactions by the electron paramagnetic resonance (EPR) technique. Complication is due to the presence of disorder in the cation positions and/or oxygen deficiency that could lead to the appearance of magnetic frustration [1-7]. Neutron diffraction studies and analysis of the crystal structure of the vanadate systems, with oxygen index x=11 and x=24, have shown that the cation disorder is more pronounced for x=11 compounds, for which the absence of a long-range magnetic order down to 10K was noticed [3,7,8]. Competition of the magnetic interactions could be related to the disorder at the positions of the iron(III) ions and/or to the oxygen deficiency [3,6]. As a result, at higher temperatures, the magnetic long-range order could not be established, inducing the appearance of magnetic frustration [3-6,9]. It has been noticed that even a small change in the annealing temperatures during synthesis could has a pronounced effect on the physical properties of these compounds [6,10].

The aim of this paper is to report on the study of the temperature dependence of the EPR spectra in the Cu$_3$Fe$_4$V$_6$O$_{24}$ system above 90K and to analyse the anomalous magnetic interactions be-

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tween the magnetic ions in the high temperature range.

2. EXPERIMENTAL

Polycrystalline multicomponent vanadate $Cu_3Fe_4V_6O_{24}$ was obtained from the solid-state reaction between 80 mol.% $FeVO_4$ and 20 mol.% $Cu_3(VO_4)_2$, according to the equation [11]:

$$4\ FeVO_4 + Cu_3(VO_4)_2 = Cu_3Fe_4V_6O_{24}.$$

$Cu_3Fe_4V_6O_{24}$ crystallizes in the triclinic system, and the values of the unit cell parameters are: a=0.6600(3) nm, b=0.8048(4) nm, c=0.9759(5) nm, α=106,08(3)°, β=103.72(3)° and γ=102.28(2)°.

The EPR spectra were recorded using a standard X-band spectrometer Bruker E 500 (ν=9.5 GHz) with magnetic field modulation of 100 kHz. The magnetic field was scaled with NMR magnetometer. The samples, containing 30 mg of the substance in the form of fine powder, were sealed into 4 mm in diameter quartz tubes. The measurements were performed in the temperature range of 90 to 290K using an Oxford nitrogen flow cryostat.

3. RESULTS AND DISCUSSION

Fig. 1 presents the EPR spectrum of the multicomponent vanadate $Cu_3Fe_4V_6O_{24}$ at room temperature. A single, almost symmetrical line dominates the EPR spectrum. It was fitted to a full Lorentzian line comprising the tail of the resonance absorp-

tion at negative fields, a consequence of the linearly polarized microwave field that becomes important when the width becomes comparable to the resonance field. The registered EPR line at room temperature is centred at g_{eff}=2.0131(3), with peak-to-peak linewidth ΔH_{pp}=109.0 mT, implying the presence of Fe^{3+} ions in the high spin d^5 state ($^6S_{7/2}$ ground state). These values are slightly different from those measured for sample $Zn_3Fe_4V_6O_{24}$ and the differences are the following: δg=0.0018 and δH_{pp}=12.2 mT [5]. Accurate fitting with a single Lorentzian line indicates that the exchange narrowing is more effective among the inequivalent Fe^{3+} sites for sample $Cu_3Fe_4V_6O_{24}$ but the position of the resonance line is shifted more in the direction of lower magnetic fields.

Fig. 2 shows the temperature dependence of representative EPR spectra of $Cu_3Fe_4V_6O_{24}$ in the whole investigated temperature range. The EPR spectra have shown the presence of a single, almost symmetrical, broad and very intense resonance line. Above 230K, with increasing temperatures, the line shifts in the direction of higher magnetic fields while an opposite shift is observed below 200K.

Figs. 3 and 4 present the temperature dependences of the following three EPR parameters: the effective g-factor, resonance field H_r, and the peak-to-peak linewidth ΔH_{pp}, all of them obtained from the fitting. Fig. 5 presents the temperature dependence of the integrated intensity I_{int}, the reciprocal of integrated intensity, and the product of integrated
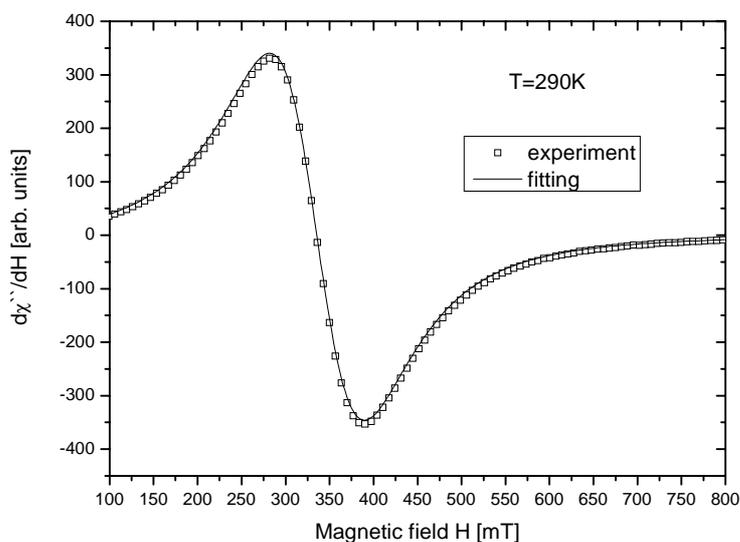

Fig. 1. The EPR spectrum of the $Cu_3Fe_4V_6O_{24}$ compound at room temperature: open squares – experimental points, solid curve – fitting by Lorentzian curve.
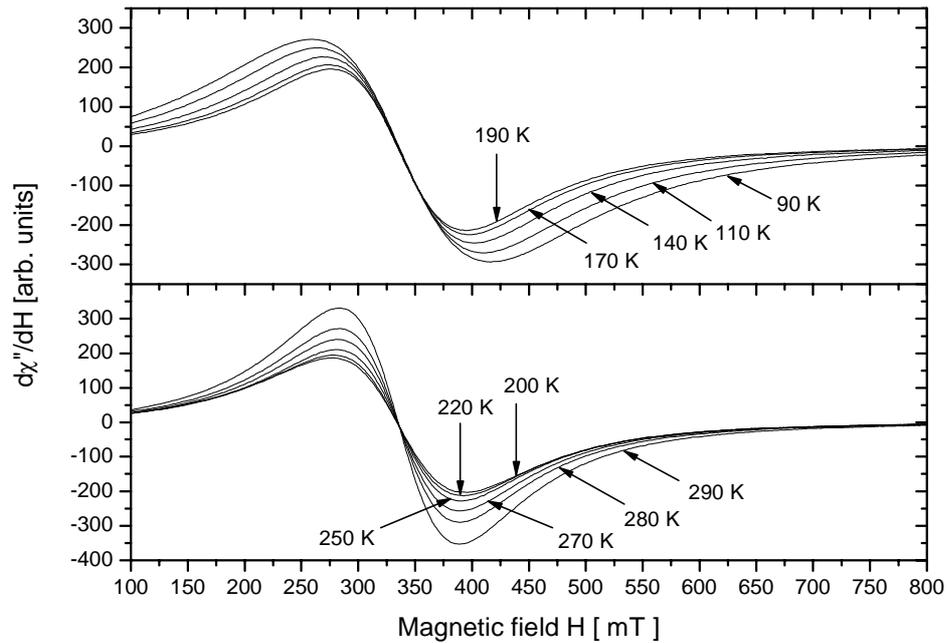
Fig. 2. The EPR spectra of the $Cu_3Fe_4V_6O_{24}$ compound at selected temperatures.

intensity and temperature. The EPR integrated intensity, I_{int}, is calculated as the product of signal amplitude and the square of the linewidth, and is proportional to the static magnetic susceptibility of the investigated sample. The temperature variation of the resonance field and the integrated intensity display a minimum at about 230K and the ratio of the resonance field change to the temperature change is different above and below this temperature, with the following values: $\Delta H/\Delta T_{>230}=1.39 \cdot 10^{-2}$ mT·K^{-1} and $\Delta H/\Delta T_{<160}=-2.69 \cdot 10^{-2}$ mT·K^{-1} ($\Delta H/\Delta T_{>230}=1.25 \cdot 10^{-2}$ mT·K^{-1} and $\Delta H/\Delta T_{<160}=-2.16 \cdot 10^{-2}$ mT·K^{-1} for sample $Zn_3Fe_4V_6O_{24}$ [5]). It is interesting to note that both these temperature gradients are greater than for a similar compound with diamagnetic Zn(II) ions but the minimum value is
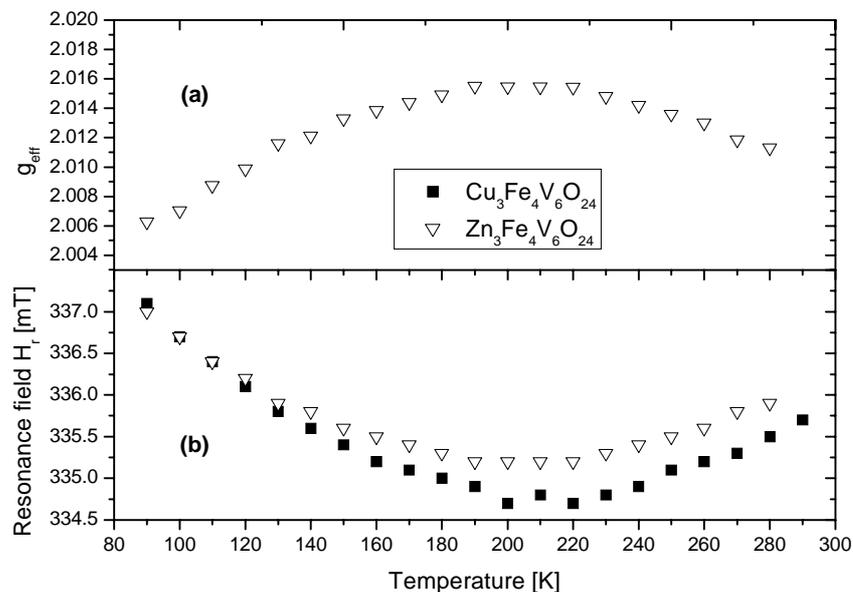

Fig. 3. The temperature dependence of the EPR parameters, (a) g_{eff}-factor, (b) resonance field H_r.
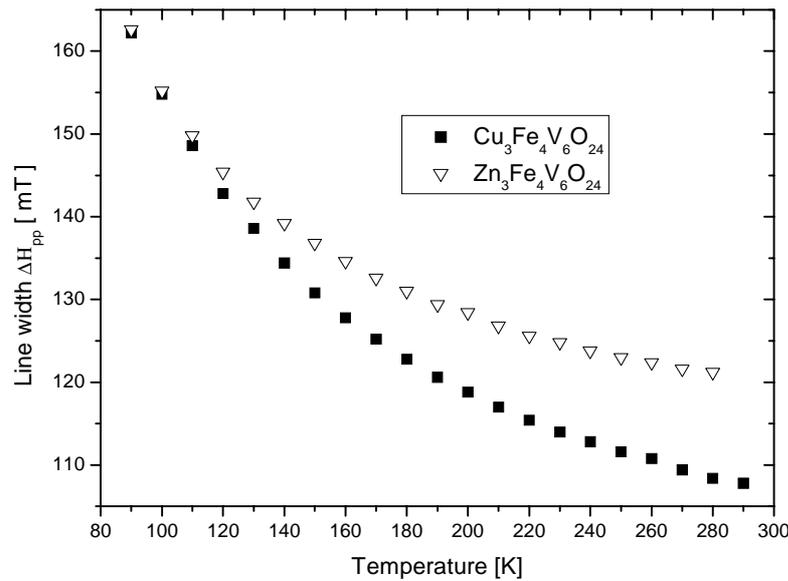
Fig. 4. The temperature dependence of the linewidth ΔH_{pp}.

observed almost at the same temperature. The differences between *g*-factors for these two compounds at this temperature is $\delta g = 0.003$ and it is assumed to be the result of replacement of non-magnetic zinc(II) by magnetic copper(II) ions (Fig. 3b). At low temperatures the shift of the resonance line is reaching the same value for both compounds. It is suggested that the magnetic interaction of iron(III) ions is stronger and could be the

dominating factor in an attempt of formation of an ordered magnetic state.

Fig. 4 gives the temperature dependence of the linewidth ΔH for samples of $Zn_3Fe_4V_6O_{24}$ and $Cu_3Fe_4V_6O_{24}$. The difference in linewidths between these two cases is increasing with temperature increase while at lower temperatures the linewidths approach the same value. The magnetic dipole interaction should more complicated for the sys-
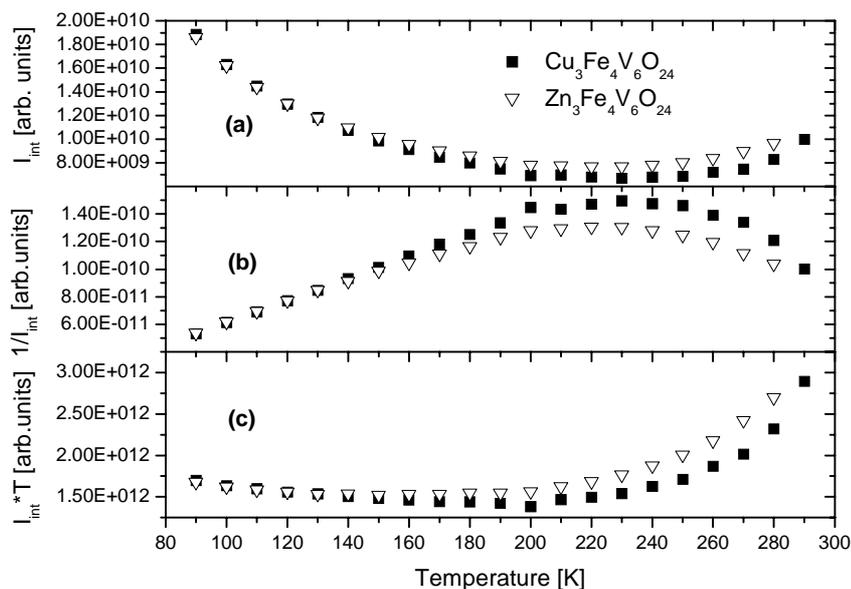

Fig. 5. The temperature dependence of: (a) integrated intensity I_{int}, (b) reciprocal integrated intensity, and (c) the product of integrated intensity and temperature.

tem with copper(II) ions and tends to broaden the line while the exchange narrowing has the opposite effect on linewidth.

Fig. 5a shows the temperature dependence of the integrated intensity for the $Zn_3Fe_4V_6O_{24}$ and $Cu_3Fe_4V_6O_{24}$ compounds. Substantial differences between those two samples are observed at high temperatures which indicate on smaller magnetic susceptibility for the system with copper(II) ions. Low temperature part of the thermal dependence of reciprocal integrated intensity for $Cu_3Fe_4V_6O_{24}$ compound shows a Curie-Weiss behaviour, $C/(T-\Theta)$, with the Curie-Weiss temperature $\Theta=25K$ (Fig. 5b). The product $I_{int}T$ is proportional to the square root of an effective magnetic moment of the investigated sample. It decreases in higher temperature as the temperature is decreased and increases slightly with decreasing temperatures below 200K. Thus it could be argued that at high temperatures the antiferromagnetic interaction operates between the spins while below 200K the magnetic interaction changes sign and becomes slightly ferromagnetic. This peculiar behaviour of the EPR parameters shows a striking similarity with that observed for materials possessing critical points and it could be associated with the phase transition to magnetically ordered state or to the spin glass state [12-14]. The presence of competing ferromagnetic and antiferromagnetic interactions was earlier observed, e.g. for insulating thiospinels $CdIn_{2-2x}Cr_{2x}S_4$ [15]. These phenomena are due to the slowing down of spin fluctuations and the change of an internal magnetic field. The observed temperature dependence of the integrated intensity is suggesting that part of the bulk material could be involved in formation of magnetic clusters and the magnetic interactions of the bulk manifest themselves in the registered EPR signal behaviour. Similar thermal conduct of the spectral parameters has been observed in the ferromagnetic resonance (FMR) of magnetic nanoparticles embedded in a diamagnetic matrix [16]. Yet another system that showed similar EPR properties is the $(Yb,Sm)Ba_2Cu_3O_{6+x}$. The EPR spectra of ytterbium(III) ions in $(Yb,Sm)Ba_2Cu_3O_{6+x}$ have been reordered at very low temperatures (about 3.4K), but it was assumed that this result should be attributed to the existence of a non-stochiometric state formed due to oxygen deficiency [17]. It is well known that the rare earths in very low temperatures order antiferromagnetically and it could be suggested that in systems with two different rare earth ions a competition of magnetic interactions is expected. These magnetic in-

teractions change the resonance condition: $h\nu=g\mu_B(H_0\pm H')$, where μ_B is the Bohr's magneton, H_0 is an external applied magnetic field and H' is an internal magnetic field created by magnetic dipoles arranged in clusters or agglomerates.

The investigated compound with coexisting sublattices of strong magnetic iron(III) ions and weak magnetic copper(II) ions could form a complicated network of magnetic interactions. The iron sublattice would aim to order independent from the other subsystem, what would induce competition of magnetic interactions, and in consequence lead to magnetic frustration.

Another interpretation of the changing shift of the resonance line involves formation of an internal magnetic field by the dipole-dipole interaction of clusters or agglomerates. If the effect of the geometrical term ($<3\cos^2\Theta-1>$) in an expression of the dipole field is considered, it could be seen that this term changes sign when the angle Θ is properly changed. If that angle is temperature dependent, it could provide suitable explanation of the observed shift of the resonance line. In general, the shift of a resonance line is often the consequence of an attempt to form magnetic ordered state. The studied material belongs to the multiphase magnetic system, in which the frustration phenomena are usually destructive for such ordering.

The crystal structure of $Cu_3Fe_4V_6O_{24}$, like other $M_3Fe_4V_6O_{24}$ compounds, is build up of $M(1)O_6$ polyhedra, $M(2)O_5$ trigonal bipyramids, $M(3)O_6$ and $M(4)O_6$ octahedra and isolated VO_4 tetrahedra. Fe_2O_{10} octahedral dimers alternate with $M(2)O_5$ bipyramids to form edge-sharing chains (Fe(1) and Fe(2) are in position M(3) and M(4), respectively). The $M(1)O_6$ octahedra are located between the chains and share corners with both the $M(2)O_5$ and Fe_2O_{10} units. The distance between Cu(1) ions in $Cu_3Fe_4(VO_4)_6$ is greater than between Fe(1) and Fe(2) octahedra forming the edge-sharing dimeric clusters. The values of the Fe(1)-Fe(1) and Fe(2)-Fe(2) distances in $Cu_3Fe_4V_6O_{24}$ compound are the following: $d_{Fe(1)-Fe(1)}=0.3095$ nm $d_{Fe(2)-Fe(2)}=0.3151$ nm [1]. These distances differ substantially and it could result in two competing magnetic interactions.

In conclusion, the polycrystalline multicomponent vanadate $Cu_3Fe_4V_6O_{24}$ with magnetic copper (II) ions has been prepared for the study of the temperature dependence of the EPR (or FMR) spectra and for investigation of the influences of magnetic interactions. The temperature dependence of the magnetic resonance spectra has shown an unusual change of the parameters of the resonance

line at 230K and it is suggested that this temperature point is important for the multiphase magnetic system. The existence of competing magnetic interactions could explain the observed temperature behaviour of the magnetic resonance spectra, connected with the presence of iron(III) ions in two different magnetic sublattices with different iron(III)-iron(III) distances. The replacement of diamagnetic zinc(II) for magnetic copper(II) ion has changed essentially all magnetic resonance parameters in the high temperatures range.

ACKNOWLEDGEMENTS

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