Competing Magnetic Interactions in $Zn_3Fe_4V_6O_{24}$ Studied by Electron Paramagnetic Resonance

G. Zolnierkiewicz[a,*], N. Guskos[a,b], J. Typek[a]
and A. Blonska-Tabero[c]

[a]Institute of Physics, Szczecin University of Technology
al. Piastów 17, 70-310 Szczecin, Poland
[b]Solid State Physics, Department of Physics, University of Athens
Panepistimiopolis, 15 784 Zografos, Athens, Greece
[c]Department of Inorganic and Analytical Chemistry
Szczecin University of Technology, al. Piastów 17, 70-310 Szczecin, Poland

A multicomponent vanadate $M_3Fe_4V_6O_{24}$ sample with non-magnetic M = Zn(II) ions was synthesized by the solid state reaction method using stoichiometric mixtures of the 80mol% $FeVO_4$ and 20mol% $Zn_3(VO_4)_2$. The temperature dependence of the EPR spectra was performed in the 90–280 K temperature range. The resonance field and the integrated intensity of the EPR line showed minimum value of both parameters at $\approx$ 200 K. It is suggested that a part of the sample is displaying tendency to form an antiferromagnetic ordered state (or the magnetic clusters) above this temperature while below the ferromagnetic interaction of the main part of material is dominating. This behaviour is attributed to the inherent magnetic inhomogeneity of the system due to the presence of the ferromagnetic or antiferromagnetic spin clusters.

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1. Introduction

Multicomponent vanadate $M_2FeV_3O_{11-x}$ and $M_3Fe_4V_6O_{24-x}$ (M(II) — magnetic and non-magnetic metal ions) have displayed extraordinary physical properties, especially due to the presence of magnetic ordered states (long- or short-range order) which could be connected to disorder phenomena observed

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*corresponding author; e-mail: gzolnierkiewicz@ps.pl

in cation positions or introduced by oxygen deficiency [1–7]. Neutron diffraction study and the analysis of the crystal structure have shown that for the $Zn_2FeV_3O_{11-x}$ compound the cation disorder phenomena are more pronounced than for the $Zn_3Fe_4V_6O_{24-x}$ compound [5, 7]. The magnetic and EPR measurements of $Zn_2FeV_3O_{11-x}$ vanadate have shown that magnetic inhomogeneity arising from the high spin iron(III) ions ($3d^5$, $^6S_{5/2}$ ground state) located in different sublattices is preventing formation of the long-range ordered magnetic state at higher temperatures while the short-range magnetic clusters could exist around room temperatures [3, 6]. The temperature dependence of the EPR parameters of the $Zn_2FeV_3O_{11-x}$ vanadate oxide has confirmed the antiferromagnetic coupling of iron(III) spins at higher temperature. The long-range magnetic order building up at about ≈ 50 K was disrupted by the disorder phenomena of cation metal ions [7].

The aim of this report is to study the temperature dependence of the EPR spectra in a vanadate $Zn_3Fe_4V_6O_{24-x}$ and to analyze the magnetic interactions between magnetic ions.

2. Experimental

Polycrystalline vanadate of $Zn_3Fe_4V_6O_{24-x}$ was obtained from a solid-state reaction between 80mol% $FeVO_4$ and 20mol% $Zn_3(VO_4)_2$, according to the equation [8]:

$$4FeVO_4 + Zn_3(VO_4)_2 = Zn_3Fe_4V_6O_{24-x}.$$
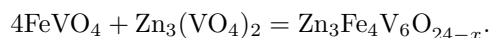
The EPR spectra were recorded using a standard X-band spectrometer type Bruker E500 ($\nu = 9.455$ GHz) with magnetic field modulation of 100 kHz. The magnetic field was scaled with a NMR magnetometer. The samples, containing 30 mg of the substance in the form of fine powder, without any cement-dielectric, were sealed into 4 mm in diameter quartz tubes. The measurements were performed in the temperature range of 90 to 280 K using an Oxford nitrogen flow cryostat and a standard hot air flow system.

3. Results and discussion

The temperature dependence of the EPR spectra of $Zn_3Fe_4V_6O_{24-x}$ vanadate in the whole range of temperatures have shown the presence of a single, almost symmetrical, broad and very intense resonance line.

Figure 1 presents EPR spectrum of the $Zn_3Fe_4V_6O_{24-x}$ vanadate at room temperature. The registered EPR line is centred at $g = 2.0113(3)$ with line width $\Delta H_{pp} = 121.2$ mT, implying the presence of Fe^{3+} ions in the high spin d^5 state ($^6S_{7/2}$ ground state).

Figure 2 shows the spectra observed at selected temperatures in the 90–280 K temperature range. To evaluate the EPR parameters, the derivative spectra were fitted to a full Lorentzian line comprising the tail of the resonance absorption at
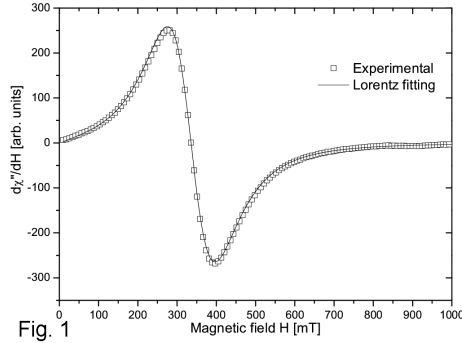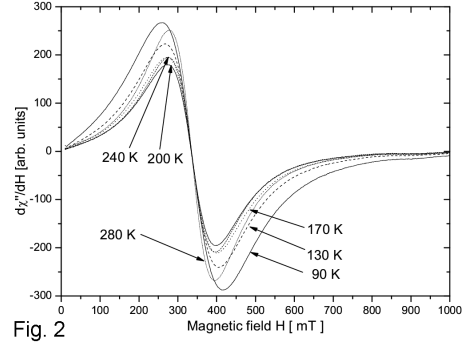
Fig. 1.   The EPR spectrum of the $Zn_3Fe_4V_6O_{24}$ compound at room temperature: open squares — experimental points, solid curve — fitting by Lorentzian curve.

Fig. 2.   The EPR spectra of the $Zn_3Fe_4V_6O_{24}$ compound at selected temperatures.

negative field, a consequence of the linearly polarized microwave field that becomes important when the width becomes comparable to the resonance field, as in the present case. Accurate fitting with a single Lorentzian line shape (Fig. 1) indicates that exchange narrowing is effective among the inequivalent Fe^{3+} sites in the whole temperature range.
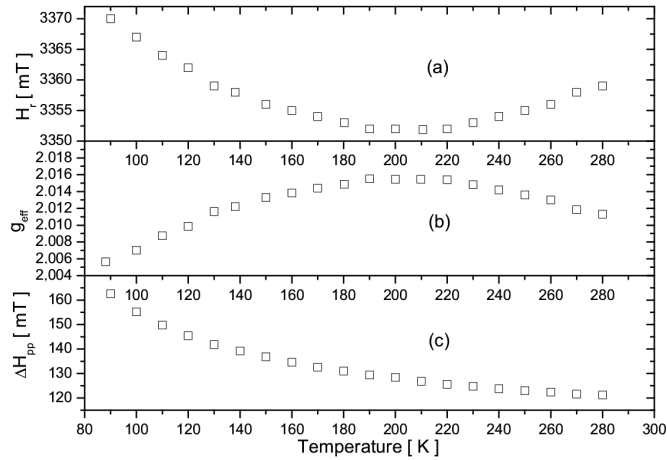

Fig. 3.   The temperature dependence of the EPR parameters: (a) resonance field H_r, (b) g_{eff} parameter, and (c) line width ΔH_{pp}.

In Fig. 3 the temperature dependences of the EPR parameters: the effective g-factor, resonance field H_r, peak-to-peak line width ΔH_{pp} are presented.

Figure 4 presents the temperature dependence of the integrated intensity, reciprocal of integrated intensity, and the product of integrated intensity and temperature. The EPR integrated intensity, I_{in}, is calculated as the product of signal amplitude and the square of the line width. It is proportional to the static mag-
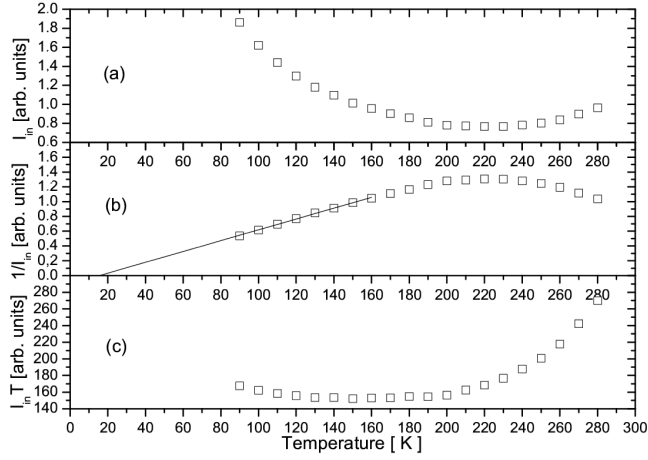
Fig. 4. The temperature dependence of: (a) integrated intensity I_{in}, (b) reciprocal integrated intensity, and (c) the product of integrated intensity and temperature.

netic susceptibility of the sample. The temperature variation of resonance field and integrated intensity is showing minimum at above 200 K and the ratio of the resonance field change to the temperature change is different above and below this temperature, with the following values: $\Delta H/\Delta T_{>200} = 1.25 \times 10^{-2}$ mT K^{-1} and $\Delta H/\Delta T_{<200} = -2.75 \times 10^{-2}$ mT K^{-1}, respectively. Low temperature part of the thermal dependence of reciprocal integrated intensity shows a Curie–Weiss behaviour $C/(T - \Theta)$ with the Curie–Weiss temperature $\Theta = 15$ K, which indicates the presence of ferromagnetic interaction. The product $I_{in}T$ is proportional to the effective magnetic moment of the sample. Figure 4c indicates that below 120 K the ferromagnetic interaction operates between the spins while above 220 K the magnetic interaction changes sign and becomes antiferromagnetic. This extraordinary behaviour of the EPR parameters observed at different temperatures could be also found in materials with critical points and is connected with the phase transitions to magnetic ordered state or to the spin glass state [9, 10]. These phenomena are due to the slowing down of spin fluctuations and the change of internal magnetic field. Similar change of the EPR parameters, with maximum resonance field and integrated intensity at $T \approx 55$ K was recorded for the vanadate $Zn_2FeV_6O_{11-x}$ [6]. The presence of competing ferromagnetic and antiferromagnetic interactions was observed, e.g. for insulating thiospinels $CdIn_{2-2x}Cr_{2x}S_4$ [11]. The observed temperature dependence of the integrated intensity is suggesting that a part of the bulk materials could be involved in antiferromagnetic clusters but the ferromagnetic interactions of the bulk are dominating the EPR signal behaviour at lower temperatures. The structure of the $Zn_3Fe_4V_6O_{24}$ vanadate contains two inequivalent Fe positions: Fe(1) and Fe(2) in FeO$_6$ octahedra. The octahedra form edge-sharing dimeric clusters. The Fe(1)–Fe(1) and Fe(2)–Fe(2) distances are the following: $d_{Fe(1)-Fe(1)} = 0.3095$ nm and $d_{Fe(2)-Fe(2)} = 0.3152$ nm [7]. These dis-

tances differ significantly and the difference could be the result of two competing magnetic interactions. Magnetic interactions could influence the resonance condition: $h\nu = g\mu_{\rm B}(H_0 \pm H')$, where $\mu_{\rm B}$ is the Bohr magneton, H_0 is an external applied magnetic field and H' is an internal magnetic field.

4. Conclusions

The $Zn_3Fe_4V_6O_{24}$ vanadate with non-magnetic zinc(II) ions was prepared for study of the magnetic interactions. The temperature dependence of the EPR spectra showed an extraordinary behaviour with a critical point at about 200 K. The behaviour of the EPR parameters (integrated intensity and resonance line shift) is suggesting the existence of competing magnetic interactions. It is very probable that the existence of two subsystems of the iron ions with different interactions (ferro- and antiferromagnetic) could explain the observed behaviour of the EPR spectra. As the iron(III) and zinc(II) ions are not disordered in the crystal structure, the oxygen deficiency is supposed to play an important role as a source of disorder that produces the two subsystems of magnetic ions.

References

[1] M.A. Lafontaine, J.M. Greneche, Y. Laligant, G. Ferey, *J. Solid State Chem.* **108**, 1 (1994).

[2] X. Wang, D.A. Vander Griend, C.L. Stern, K.R. Poeppelmeier, *Inorg. Chem.* **39**, 136 (2000).

[3] X. Wang, D.A. Vander Griend, C.L. Stern, K.R. Poeppelmeier, *J. Alloys Comp.* **158**, 119 (2000).

[4] N. Guskos, M. Wabia, M. Kurzawa, A. Bezkrovnyy, V. Likodimos, J. Typek, I. Rychlowska-Himmel, A. Blonska-Tabero, *Radiat. Eff. Defects Solids* **158**, 369 (2003).

[5] N. Guskos, J. Typek, A. Bezkrovnyy, M. Wabia, M. Kurzawa, E.A. Anagnostakis, *J. Alloys Comp.* **377**, 47 (2004).

[6] V. Likodimos, N. Guskos, S. Glenis, R. Szymczak, A. Bezkrovnyy, M. Wabia, J. Typek, G. Gasiorek, M. Kurzawa, I. Rychlowska-Himmel, A. Blonska-Tabero, *Eur. Phys. J. B* **38**, 13 (2004).

[7] N. Guskos, A. Bezkrovnyy, J. Typek, N.Yu. Ryabova, A. Blonska-Tabero, M. Kurzawa, M. Maryniak, *J. Alloys Comp.* **391**, 20 (2005).

[8] M. Kurzawa, A. Blonska-Tabero, *Mater. Res. Bull.* **37**, 849 (2002).

[9] D.L. Hubner, *Phys. Rev.* **6**, 3180 (1972).

[10] C.Y. Huang, *J. Magn. Magn. Mater.* **51**, 1 (1985).

[11] S. Viticoli, D. Fiorani, M. Nogues, J.L. Dorman, *Phys. Rev. B* **26**, 6085 (1982).