Materials Science-Poland, Vol. 24, No. 4, 2006

Effects of thermal treatment on magnetic properties of $Ni_2FeV_3O_{11-\delta}$ compound

N. GUSKOS[1, 2*], J. TYPEK[2], G. ŻOŁNIERKIEWICZ[2],
A. BŁOŃSKA-TABERO[3], S. LOS[4], W. KEMPIŃSKI[4]

[1]Solid State Section, Department of Physics, University of Athens,
Panepistimiopolis,15 784 Zografos, Athens, Greece

[2]Institute of Physics, Szczecin University of Technology, al. Piastów 17, 70-310 Szczecin, Poland

[3]Institute of Chemistry and Environmental Protection,
Szczecin University of Technology, al. Piastów 42, 71-065 Szczecin, Poland

[4]Institute of Molecular Physics, Polish Academy of Sciences,
Smoluchowskiego 17, 60-179 Poznań, Poland

$Ni_2FeV_3O_{11-\delta}$ samples have been synthesized by the solid-state reaction method using two different heat treatment processes (samples of the type A and B). The XRD measurements have shown the same diffraction patterns for both types of samples. The temperature dependences of the electron paramagnetic resonance (EPR) spectra have been recorded for the two types of thermal annealing processes of $Ni_2FeV_3O_{11-\delta}$. Strong differences have been observed in the EPR spectra of both types of $Ni_2FeV_3O_{11-\delta}$. An intense EPR line has been recorded at high temperatures; it is suggested that the line is associated with oxygen–vanadium clusters (ferromagnetic ordering). The linewidth, resonance field and integrated intensity of the EPR spectra have shown a strong temperature dependence down to 200 K. Additionally, in one sample a very broad EPR line of Fe^{3+} ions appeared at low temperatures while at high temperatures this line was overlapped by the other line. The temperature dependence of the integrated intensity of this broad line has shown the Curie–Weiss behaviour. In the vanadate oxide materials with two strong magnetic ions in the structure (iron(III) and nickel(II)), the spectrum of the Fe^{3+} ions is not observed. Different oxygen deficiency processes could explain the differences in the EPR spectra of both types of $Ni_2FeV_3O_{11-\delta}$ compounds.

Key words: *EPR; vanadate oxide; oxygen deficiency*

1. Introduction

Recently, very strange physical properties have been reported in some insulating vanadates and, in consequence, they have been very intensively studied [1–6]. The disorder of iron and metal atoms revealed in the structural studies of multicomponent

---

[*] Corresponding author, e-mail: ngouskos@phys.uoa.gr

vanadates $Me_2FeV_3O_{11-x}$ (Me = Zn and Mg) could be responsible for significant differences observed in their physical properties [5–7]. The temperature dependences of the EPR spectra of the polycrystalline vanadium oxides $Ni_2FeVO_{6-\delta}$ and $Zn_2FeV_3O_{11-\delta}$ have been investigated [8, 9]. For $Ni_2FeVO_{6-\delta}$, an intense EPR line associated with ferromagnetic clusters in the Fe–V layers were observed. Strong temperature dependences of its linewidth, resonance field and intensity have also been found in magnetic susceptibility measurements. For $Zn_2FeV_3O_{11-\delta}$, a very broad and intense EPR line originating from the high-spin iron(III) ions has been recorded and at about 50 K, an influence of the dynamical spin fluctuation on the EPR line has been observed [9].

The polycrystalline nickel–iron–vanadium oxide (Ni–Fe–V–O system) is a very interesting subject of extensive experimental investigations, due to its various magnetic interactions associated with the magnetic frustration induced by three oxidation states of the vanadium ion. $Ni_2FeVO_{6-\delta}$ crystallizes in the rhombohedral $FeTiO_3$-type (ilmenite) structure, comprising alternate metal layers forming a two-dimensional magnetic structure. It was assumed to be a ferrimagnet with a high Neel temperature and feeble magnetocrystalline anisotropy [10]. The hexagonal structural layers of nickel ions with antiferromagnetic ordering are expected not to essentially influence magnetic properties of this system. In the stoichiometric compound ($\delta = 0$) every other site is expected to be occupied by the Fe^{3+} ions separated by diamagnetic V^{5+} ions, with positive superexchange interactions. The magnetic moment obtained from the temperature dependence of the magnetic susceptibility is much smaller than for the ideal magnetic structure. Additionally, observed remarkable singularities suggest that different magnetic interactions operate in this system [1, 3]. Vanadium ions exhibit three main valence states: V^{3+} (spin $S = 1$), V^{4+} ($S = 1/2$) and V^{5+} ($S = 0$) due to oxygen deficiency with main contribution of the V^{5+} ions for $\delta = 0$. Thus modifying the Fe–Fe interactions could lead to the coexistence of various magnetic phases. A qualitative description of the magnetisation curve has been attempted in terms of the Ising model with random-bond quenched disorder reflecting the distorted Fe–Fe bonds by randomly distributed V ions with different valence states [10]. Thus it is suspected that for systems containing more vanadium ions at various oxidation levels the magnetic interactions could be more interesting.

In the present work, the $Ni_2FeV_3O_{11-\delta}$ compound, where every fourth site is expected to be occupied by Fe^{3+} ions separated by diamagnetic V^{5+} for the stoichiometric compound ($\delta = 0$) by two different thermal annealing regimes, has been prepared. EPR experiments have been carried out in order to trace intrinsic magnetic centres with frustration phenomena and to obtain a further insight into its complex magnetic properties resulting from various oxygen deficiency processes the samples were subjected to.

2. Experimental

The polycrystalline $Ni_2FeV_3O_{11-\delta}$ samples used in this study have been obtained by the solid-state reaction method [11]. Two different thermal annealing programmes have been used for preparation of this compound. The first type of sample (sample A) has been synthesised from vanadates, according to the equation:

$$FeVO_4 + Ni_2V_2O_7 = Ni_2FeV_3O_{11}$$

During the synthesis, the powdered mixture was thermally annealed for 24 h at 913 K and for 24 h at 1073 K. The thermal annealing process was different from that proposed by Melentev et al. [12]. The second type of sample (sample B) was synthesized as follows: the mixture of oxides (NiO, 50.00 mol %, V_2O_5, 37.50 mol %, and Fe_2O_3, 12.50 mol %) was annealed in air atmosphere at 873 K during 24 hours (twice). Then the pellet was thermally annealed at 923 K during 24 hours (twice) and $Ni_2FeV_3O_{11}$ compound was synthesized according to the reaction:

$$4NiO + 3V_2O_5 + Fe_2O_3 = 2Ni_2FeV_3O_{11}$$

The obtained compound has a blackish-brown colour, with the melting point 1208 K (in contrast to 1238 K for the same compound obtained by Melentev et al. [12]) and with $Ni_3V_2O_8$ and $NiFe_2O_4$ stable decomposition products [12].

Sample identification by the X-ray powder diffraction revealed the presence of the phase with triclinic symmetry and with the following unit cell parameters: a = 0.8818(2) nm, b = 0.7582(2) nm, and c = 0.7023(3) nm, α = 117.06(3)°, β = 89.44(4)°, γ= 105.35(2)°, Z = 2 [11]. The experimentally determined density value is d = 4.21(5) g/cm^3, and is in a reasonable agreement with the X-ray density of d_{rtg} = 4.17 g/cm^3.

The EPR spectra were recorded using a conventional X-band spectrometer BRUKER E 500 with the magnetic field modulation of 100 kHz. The magnetic field was scaled with the usual NMR technique. The sample, containing 30 mg of the material in the form of fine powder was placed into a 2 mm diameter quartz tube. The measurements were done in the temperature range from 4.2 K to 300 K using an Oxford Instrument flow cryostat.

3. Results and discussion

Figure 1 presents the temperature dependence of the EPR spectra for the samples A and B. The corresponding EPR spectra at high temperatures consist of a single, slightly asymmetric EPR line, of an almost Lorentzian lineshape, typical of the exchange narrowed systems in the sample A and an additional very wide line in the sample B. In both cases, strong temperature dependences of all EPR parameters (I – integrated intensity, defined as the product of line amplitude and square of linewidth, ΔB – peak-to-peak linewidth and B_r – resonance field) are observed. The EPR line for the sample A has been well fitted with the Lorentzian lineshape in the investigated temperature range (Fig. 2a).

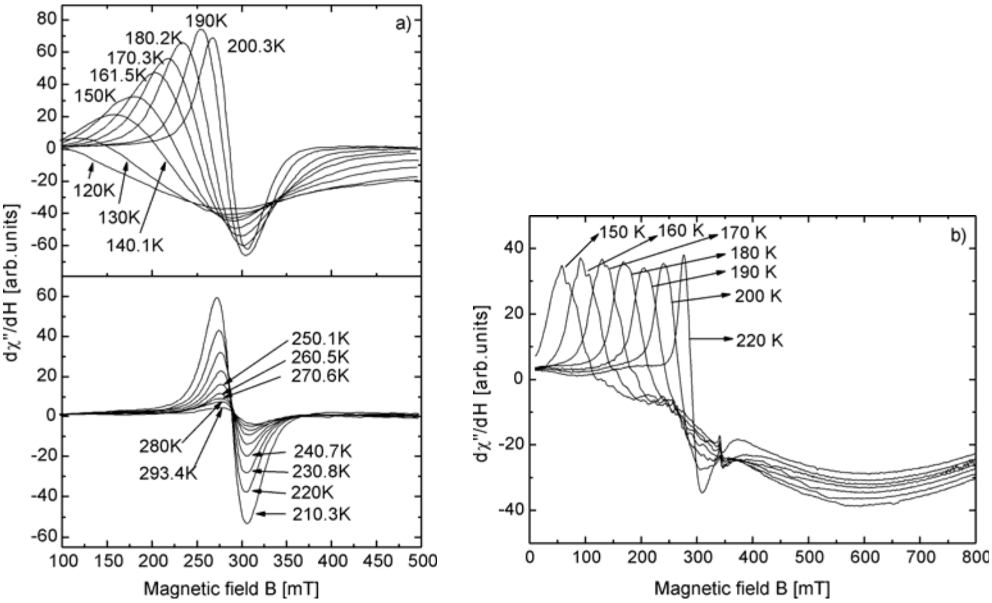

Fig. 1. The EPR spectra for the sample A (a), and B (b), at selected temperatures

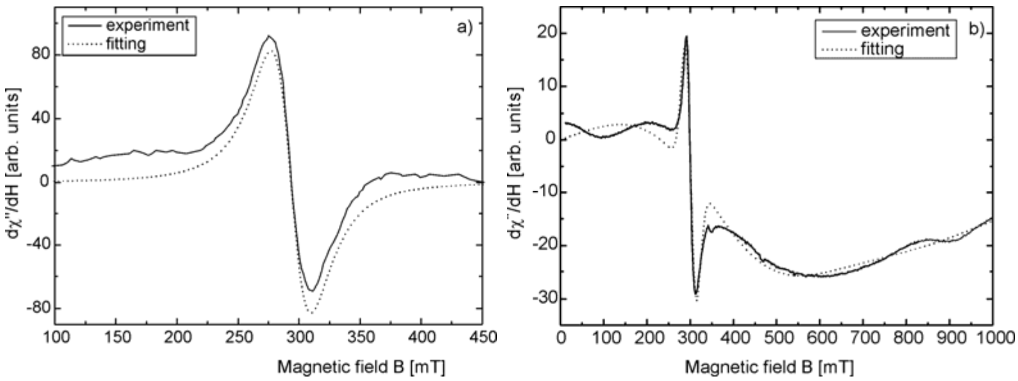

Fig. 2. Comparison of the experimental (solid line) and fitted (dashed line) EPR spectra for the sample A (a) and sample B (b), at 270 K

The EPR line for the sample B has been approximated by two Lorentzian lines, one narrow, similar to the line observed in the sample A and the other very broad, arising probably from the iron(III) ions (Fig. 2b).The resonance field of the broad component is almost constant in the whole investigated temperature range and the line is probably due to the spurious phases present in a very small amount in the samples. At room temperature, a narrow line is centred at 294 mT (corresponding to the effective *g*-factor ≈ 2.24), with the linewidth ΔB = 31.3(3) mT, for the sample A, and at 330 mT ($g \approx 2.00$), with the linewidth ΔB = 30.2(3) mT, for the sample B. A slight difference was observed between both samples as the EPR intensity and linewidth of this line is concerned. The temperature dependence of the integrated intensity of the EPR narrow line, $I(T)$, which is proportional to the spin susceptibility, is very weak for both samples at higher temperatures ($T > 160$ K). The value of the linewidth ΔB at high temperatures and the temperature dependence of the integrated intensity $I(T)$ down to 195–200 K is similar for both samples. Below this temperature, a strong temperature-dependent shift of the resonance field in the direction of lower magnetic fields is observed (Fig. 3) in both samples and the ratio of the change of magnetic field δB with temperature has the following values: $\delta B/\Delta T \approx 0.0709$ mT/K at high temperatures (above 200 K) and $\delta B/\Delta T \approx 1.69$ mT/K at lower temperatures for the sample A, while for the sample B $\delta B/\Delta T = 3.74$ mT/K at lower temperatures, this value being over twice greater than that for the sample A. This EPR line disappears below 110–130 K in both cases or is overlapped by a very broad EPR line from the Fe^{3+} ions. This may suggest that the dipole–dipole (or exchange) interactions and the dynamical fluctuations of the spins essentially depend on thermal treatment processes.

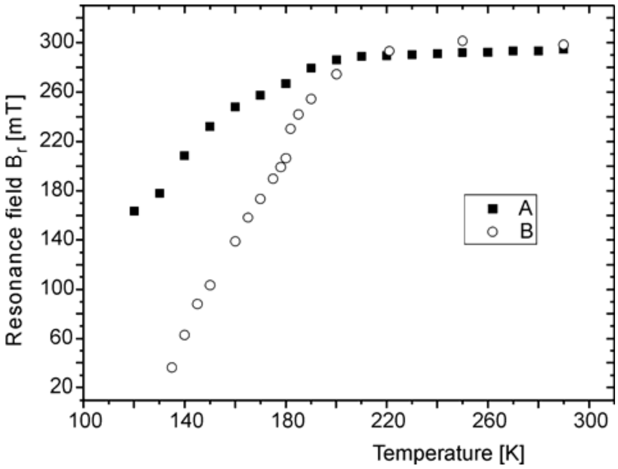

Fig. 3. Temperature dependence of the resonance field $B_r(T)$ of the narrow EPR line in the sample A (full squares) and sample B (empty circles)

The temperature behaviour of the integrated intensity complies with the corresponding temperature variation of the magnetic susceptibility curve at higher temperature, indicating that the observed EPR spectrum probes the bulk magnetic processes. In the sample A, the EPR line is more intense than in the sample B that at higher temperatures coexists with a broad EPR line originating from the Fe^{3+} ions. Above 200 K, the g parameter, the linewidth ΔB and the resonance field are almost constant in both samples. Below 200 K, for both samples the linewidths begin to increase very strongly and the resonance field shifts towards lower magnetic fields (Fig. 3). An excessive broadening of the EPR linewidths for both samples is observed at low temperatures. The amplitude of the resonance line reaches the maximum in the same temperature range (Fig. 4) in which the shift of the resonance line starts to increase strongly with the decreasing temperature.

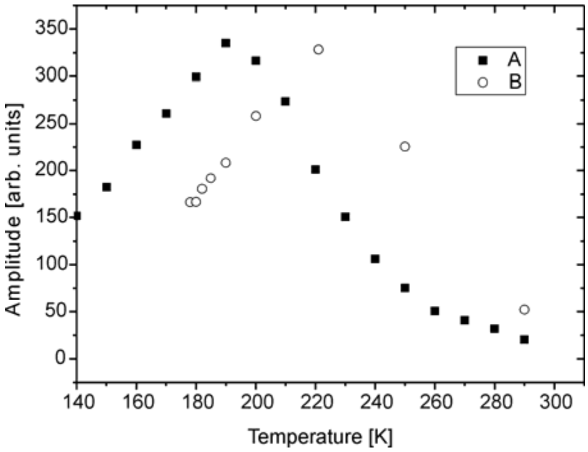

Fig. 4. Temperature dependence of the EPR signal amplitude for the sample A (full squares) and sample B (empty circles)

An interesting behaviour of the temperature dependence of *I*(T) is observed in the high-temperature region. Below 220 K, a rapid increase of ΔB is observed implying the onset of the critical fluctuations near the corresponding phase transition. The resonance field exhibits a relatively small decrease as temperature decreases down to ca. 200 K. The temperature dependence of the EPR parameters in the sample $Ni_2FeVO_{6-\delta}$ shows an almost same behaviour at higher temperatures [8]. The temperature behaviour of the EPR line of Fe^{3+} ions is in agreement with the results of magnetic measurements that indicate the presence of a certain amount of high-spin iron ions not taking part in the magnetic interaction at high temperatures. In a system containing no vanadium ions, e.g. α-Fe_2WO_6, the EPR spectrum is dominated by a line from iron(III) ions and usually at high temperatures the line is very broad [13] and near the critical temperature it displays a very interesting behaviour. A new vanadate compound, $Fe_8V_{10}W_{16}O_{85}$, has recently been investigated by the EPR method [14] and the origin of its EPR spectrum at high temperatures is still unclear.

The temperature dependence of FMR (ferromagnetic resonance) spectra of magnetic nanoparticles embedded in non-magnetic matrices, recorded with an EPR spectrometer, showed a behaviour similar to that observed for the investigated samples [15, 16]. Thus it is suggested that for the samples A and B the spectra are associated with the fraction of iron(III) ions becoming ferromagnetically ordered in small clusters. The spectrum recorded with an EPR spectrometer is therefore of the ferromagnetic resonance type because it originates not from separate spins but from a group of magnetically coupled ions. The magnetic clusters would produce the FMR absorption. The resonance condition in the presence of ferromagnetic clusters is modified by an internal magnetic field B_{int}:

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

where B_{int} could be connected with the shift of resonance FMR line and thus described by the following relation:

$$B_{\text{int}} = B_0(1 - \alpha\Delta T) \tag{2}$$

where B_0 is an external applied magnetic field, μ_B is the Bohr magneton, and α is the gradient of the change of magnetic field with temperature. The strong increase of $\delta B/\Delta T$ observed below 200 K could be connected with freezing of the magnetic cluster at this critical temperature. Then from Eqs. (1) and (2) one gets:

$$h\nu = g\mu_B B_0 \alpha\Delta T \tag{3}$$

The value of α could depend on the size of magnetic clusters because it describes the value of the internal magnetic field. For the investigated samples, the following values were calculated: $\alpha = 1.1(1)\cdot 10^{-2}$ K^{-1} for the sample A, and $\alpha = 1.3(1)\cdot 10^{-2}$ K^{-1} for the sample B.

For $Me_2FeV_3O_{11-x}$ (Me = Zn or Mg) compounds containing only one magnetic metal ion, the EPR spectra of high-spin iron(III) ion have been recorded [17, 9] while for compounds with a sublattice having two different magnetic ions the EPR spectra from Fe^{3+} ions have not been observed.

4. Conclusions

It has been shown that for the compound $Ni_2FeV_3O_{11-\delta}$ the ferromagnetic resonance spectra dominate the magnetic response and they are associated with the presence of ferromagnetic clusters in the Fe–V layers and the high-spin iron centres. A strong temperature dependence of the FMR spectra is observed with a substantial shift of the resonance lines towards lower magnetic fields. The signal disappears below 110 K in the sample A and 130 K in the sample B. A new coefficient $\delta B/\Delta T$ describing the shift of the resonance lines with temperature was introduced and calculated for both types of samples. The preparation method and thermal annealing processes strongly influence the observed FMR spectra, recorded with the EPR spectrometer.

Acknowledgements

This work has been financed from the means designed for science for years 2005–2008 as a scientific project 1311/T09/2005/29.

References

[1] SCHMIDT S., PALME W., LUTHI B., WEIDEN M., HAUPTMANN R., GEIBEL C., Phys. Rev. B, 57 (1998), 2687.

[2] KOROTIN M.A., ELFIMOV I.S., ANISIMOV V.I., TROYER M., KHOMSKII D.I., Phys. Rev. Lett., 83 (1999), 1387.

[3] LOHMANN M., KRUG VON NIDDA H.A., LOIDL A., MORRE E., DISCHNER M., GEIBEL C., Phys. Rev. B, 61 (2000), 9523.

[4] TRINKL W., LOIDL A., KLEMM M., HORN S., Phys. Rev. B, 62 (2000), 8915.

[5] WANG X., VANDER GRIEND D.A., STERN C.L., POEPPELMEIER K.P., J. Alloys Comp., 298 (2000), 119.

[6] GUSKOS N., WABIA M., KURZAWA M., BEZKROVNYI A., LIKODIMOS V., TYPEK J., RYCHLOWSKA -HIMMEL I., BLONSKA-TABERO A., Radiat. Eff. Defects Solids, 158 (2003), 369.

[7] GUSKOS N., TYPEK J., BEZKROVNYI A., WABIA M., KURZAWA M., ANAGNOSTAKIS E.A., GASIOREK G., J. Alloys Comp., 377 (2004), 47.

[8] GUSKOS N., LIKODIMOS V., LOS S., KEMPINSKI W., STANKOWSKI J., WABIA M., TYPEK J., BLONSKA -TABERO A., TABERO P., RYCHLOWSKA-HIMMEL I., Physica B, 284–288 (2000), 1456.

[9] LIKODIMOS V., GUSKOS N., GLENIS S., SZYMCZAK R., BEZKROVNYI A., WABIA M., TYPEK J., GASIOREK G., KURZAWA M., RYCHLOWSKA-HIMMEL I., BLONSKA-TABERO A., Eur. Phys. J. B, 38 (2004), 13.

[10] KOLPAKOWA L., PIETRZAK J., LATOSInSKA J.N., PAWLICKI P., J. Magn. Magn. Mater., 140 (1995), 1583.

[11] KURZAWA M., BLONSKA-TABERO A., RYCHLOWSKA-HIMMEL I., TABERO P., Mat. Res. Bull., 36 (2001), 1379.

[12] MELENTEV A.B., SURAT L.L., FOTIEV A.A., SUVOROVA G.A., SIRINA T.P., Zh. Neorg. Khim., 33 (1988), 2149.

[13] GUSKOS N., TYPEK J., WABIA M., LIKODIMOS V., FUKS H., RYCHLOWSKA-HIMMEL I., WALCZAK J., Appl. Magn. Res., 14 (1998), 397.

[14] GUSKOS N., LIKODIMOS V., PATAPIS S.K., TYPEK J., WABIA M., FUKS H., GAMARI-SEALE H., WALCZAK J., RYCHLOWSKA-HIMMEL I., BOSACKA M., J. Solid State Chem., 137 (1998), 223.

[15] KOSKAROV YU.A., PANKRATOV D.A., GUBIN S.P., KOSOBUDSKY I.D., BELTRAN M., KHODORKOVSKY Y., TISHIN A.M., J. Appl. Phys., 89 (2001), 2293.

[16] GUSKOS N., ANAGNOSTAKIS E.A., LIKODIMOS V., BODZIONY T., TYPEK J., MARYNIAK M., NARKIEWICZ U., KUCHAREWICZ I., J. Appl. Phys., 97 (2005), 024304.

[17] GUSKOS N., WABIA M., LIKODIMOS V., TYPEK J., KURZAWA M., BLONSKA-TABERO A., RYCHLOWSKA -HIMMEL I., Mol. Phys. Rep., 36 (2002), 27.

Received 9 September 2005
Revised 7 November 2005