

MAGNETIC AND DIELECTRIC STUDY OF $\text{Ni}_2\text{FeV}_3\text{O}_{11-\delta}$

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Abstract. The magnetic and dielectric properties of the $\text{Ni}_2\text{FeV}_3\text{O}_{11-\delta}$ compound synthesized using different annealing routes have been studied by means of static magnetization, electron paramagnetic resonance and dielectric spectroscopy. The temperature dependence of the magnetic susceptibility has shown marked singularities due to the coexistence of many kinds of magnetic interactions. Dielectric measurements have shown a second order phase transition to the ferroelectric state at about 200K. Dielectric loss measurements have shown an intense peak at the same temperature with activation energy of about 0.42 eV. All investigated compounds of the M-Fe-V-O (M=Ni, Zn, Mg) system have displayed a slight anomaly of the EPR parameters at about 200K. This anomaly is interpreted as arising from the competition between different magnetic subsystems preventing the formation of a long-range magnetic order.

1. INTRODUCTION

The crystal structure of the multicomponent $\text{M}_2\text{FeV}_3\text{O}_{11-\delta}$ (M=Zn(II) and Mg(II)) and $\text{M}_3\text{Fe}_4\text{V}_6\text{O}_{24-\delta}$ (M=Zn(II), Mg(II) and Mn(II)) vanadates is characterized by the presence of different metal sub-lattices and cation or oxygen disorder [1-7]. A disordered distribution of diamagnetic M(II) and high spin Fe(III) ions could influence the magnetic homogeneity of these systems, which has been detected in the temperature dependence of the magnetic susceptibility and the temperature variation of the electron paramagnetic resonance (EPR) spectra [8,9]. For a more "simple" system Ni_2FeVO_6 , the coexistence of various magnetic phases arising from different oxidation states of vanadium cations

was suggested and the formation of a magnetically ordered state below 200K was proposed based on magnetization measurements [10,11]. The temperature dependence of the EPR spectra has shown a strong variation of all the EPR parameters (linewidth, resonance field and intensity) below 200K [12]. The temperature dependence of the FMR spectra for the $\text{Ni}_2\text{FeV}_3\text{O}_{11}$ system has shown a sharp change, while the shift of the resonance field below 200K has indicated strong magnetic correlations between the high-spin state iron(III) ions [13]. A very broad and intense EPR line of the high-spin iron(III) ions has been recorded for the $\text{M}_2\text{FeV}_3\text{O}_{11-\delta}$ (M=Zn(II) and Mg(II)) compounds, where a slight change in the resonance line shift was observed at 200K followed by a sharp

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variation near 50K influenced by the dynamical spin fluctuation of iron(III) ions [8,9]. Moreover, EPR measurements of the $\text{Zn}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ compound have shown a shallow minimum in the resonance line shift at 200K [14].

In the present work, two samples of the $\text{Ni}_2\text{FeV}_3\text{O}_{11-\delta}$ compound prepared by different methods, have been investigated by magnetic, dielectric and EPR measurements in order to get further insight on its complex physical properties responsible for the anomalies observed at 200K in the M-Fe-V-O system.

2. EXPERIMENTAL

The polycrystalline $\text{Ni}_2\text{FeV}_3\text{O}_{11-\delta}$ samples have been synthesized using the solid-state reaction method [15]. Two different thermal annealing programs for the preparation of this compound have been used. The first type of sample (designated as sample A) has been synthesized from vanadates, according to the equation: $\text{FeVO}_4 + \text{Ni}_2\text{V}_2\text{O}_7 = \text{Ni}_2\text{FeV}_3\text{O}_{11}$. During this synthesis the powder mixture was thermally annealed for 24 h at the temperature 640 °C (913K) and for 24 h at 800 °C (1073K). This thermal treatment was different from that proposed by Melentev *et al.* [16]. The second type of sample (designated as sample B) was synthesized in another way. Firstly, a mixture of oxides (50.00 mol.% NiO, 37.50 mol.% V_2O_5 , and 12.50 mol.% Fe_2O_3) was heated in air atmosphere at 600 °C (873K) during 24 hours (twice). During the next stage the pellet was thermally annealed at 650 °C (923K) during 24 hours (twice). In this condition, $\text{Ni}_2\text{FeV}_3\text{O}_{11}$ compound was synthesized according to the reaction: $4\text{NiO} + 3\text{V}_2\text{O}_5 + \text{Fe}_2\text{O}_3 = 2\text{Ni}_2\text{FeV}_3\text{O}_{11}$. The obtained compound has a blackish-brown color, with a melting temperature 935(5) °C (1208K) (in contrast to 965(5) °C (1238K) for the same compound obtained by Melentev *et al.* [16]) and with $\text{Ni}_3\text{V}_2\text{O}_8$ and NiFe_2O_4 stable decomposition products [15].

Sample identification by X-ray powder diffraction showed 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, $\alpha=117.06(3)^\circ$, $\beta=89.44(4)^\circ$, $\gamma=105.35(2)^\circ$, $Z=2$ [11]. The experimentally determined density value is $d=4.21(5)$ g/cm³, which is in reasonable agreement with the Roentgen density of $d_{\text{rig}}=4.17$ g/cm³.

The EPR spectra were recorded using a conventional X-band spectrometer BRUKER E 500, with magnetic field modulation of 100 kHz. The sample, containing 30 mg of substance in the form

of fine powder was placed into a 3 mm diameter quartz tubes. The measurements were done in the temperature range from 150 to 250K using an Oxford Instrument flow cryostat. Magnetization measurements were performed on a SQUID model MPMS by Quantum Design, operating in the 1.8-400K temperature range and in 0-5.5 T range of magnetic fields.

Dielectric measurements (complex dielectric permittivity $\epsilon^* = \epsilon' - i\epsilon''$) have been performed using a Hewlet-Packard impedance analyzer HP 4192A, a digital temperature controller Shimaden SR-25 (temperature stabilization within ± 0.1 deg), a homemade sample chamber cooled down to 150K by liquid nitrogen, and a PC computer with PC-IB board for control and data storage. The temperature step was 5K, and measurements were done in the isothermal regime in the frequency range of 1 kHz to 1000 kHz in logarithmic scale (20 points per decade).

3. RESULTS AND DISCUSSION

Fig. 1 shows the temperature dependence of the effective magnetic moment (μ_{eff} /f.u.) for samples A and B at magnetic field $H=2$ kOe, compared to the corresponding temperature dependence of μ_{eff} for $\text{Ni}_2\text{FeVO}_{6-\delta}$. At high temperatures, the effective moment is about 7.3 m_B/mole, which is close to that expected per formula unit ($\delta=0$) for paramagnetic Ni^{2+} and Fe^{3+} ions. At $T < 210\text{K}$, a rapid increase of μ_{eff} is observed for sample A that is similar to the ferromagnetic transition of the $\text{Ni}_2\text{FeVO}_{6-\delta}$ compound, while a small kink is also detected at $T \approx 200\text{K}$ for sample B. Below 10K, a weak peak in the magnetic susceptibility indicates the presence of anti-ferromagnetic ordering for both samples A and B. EPR measurements showed the presence of ferromagnetic resonance (FMR) for samples A and B below 200K, where a strong shift of the resonance line towards low magnetic fields was recorded [13]. Fig. 2a shows the temperature dependence of the resonance field in the region of 150 to 250K for the three compounds, which exhibits a drastic change of the temperature derivative dH_r/dT at $T < 200\text{K}$. The temperature dependence of resonance line of iron(III) ions in the multicomponent vanadates $\text{M}_2\text{FeV}_3\text{O}_{11-\delta}$ ($M=\text{Zn(II)}$ and Mg(II)) and $\text{M}_3\text{Fe}_4\text{V}_6\text{O}_{24-\delta}$ ($M=\text{Zn(II)}$ and Mn(II)) has shown similar behavior at 200K (Fig. 2b).

Probably an intense magnetization in $\text{Ni}_2\text{FeVO}_{6-\delta}$ sample overlap the peak observed at about 200K for samples A and B. Iron ions provide the most important contribution to the magnetization curve

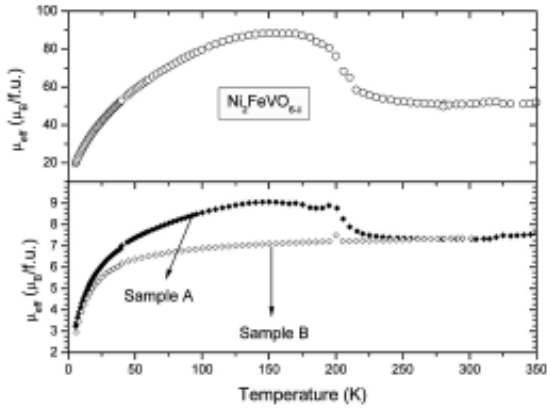


Fig. 1. Temperature dependence of the effective magnetic moments for $\text{Ni}_2\text{FeVO}_{6-\delta}$ (top panel) and samples A, B of $\text{Ni}_2\text{FeV}_3\text{O}_{11-\delta}$ (lower panel).

($S=5/2$). The subsequent layers of magnetic moments are well separated; therefore their interaction may be neglected in comparison with the interlayer interaction, since antiferromagnetically ordered nickel ions do not contribute to the spontaneous magnetization. It is sufficient to take into account the two-dimensional structures formed by vanadium and iron ions to explain certain parts of magnetic behavior. The analysis χ vs. T curve at higher temperature and use of a simple relation for $\delta=0$ enabled the calculation of the effective values of magnetic momentum of $\sim 4.9 \mu_B$ for sample $\text{Ni}_2\text{FeVO}_{6-\delta}$ and of $\sim 4 \mu_B$ for sample $\text{Ni}_2\text{FeV}_3\text{O}_{11-\delta}$. These values are smaller than expected for the high spin state of free trivalent iron ions. The fact that the vanadium ions exhibit three types of valence could be very important in discussing magnetic interactions, especially for a sample with oxygen deficiency. On the other hand the decrease of effective magnetic momentum could be caused because some iron(III) ions are in the low spin state or ferromagnetic cluster iron-oxygen-vanadium are formed. The peak of the magnetic susceptibility at $T \approx 200\text{K}$ clearly indicates the presence of ferromagnetic interactions, which could be due to the existence of ferromagnetic clusters. In that case, the distortion of the Fe-Fe bonds by random distribution of V ions with different valence states would be more severe in samples A and B than for sample $\text{Ni}_2\text{FeVO}_{6-\delta}$.

The corresponding FMR spectra at high temperatures consist of a single, slightly asymmetric FMR line, with almost Lorentzian lineshape, typi-

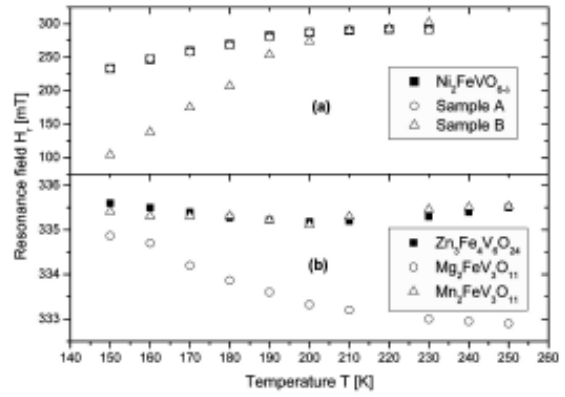


Fig. 2. Temperature dependence of the resonance field H_r in the range of 150-250K for various multi-component M-Fe-V-O vanadates.

cal of exchange-narrowed systems [13]. The integrated intensity $I(T)$ of the EPR spectrum (which is proportional to the spin susceptibility) is the same for both sample A and B at higher temperatures. The temperature behavior of the integrated intensity complies with the corresponding temperature variation of the magnetic susceptibility curve at high temperatures, indicating that the observed EPR spectrum probes the bulk magnetic behavior. For sample A the EPR line has higher amplitude than for sample B and at high temperatures coexists with a broad EPR line arising from Fe^{3+} ions. Above 220K the g parameter, linewidth ΔB , and resonance field are almost constant for both samples. Below 220K the linewidth begins to increase very strongly and the resonance field shifts towards low magnetic fields for both samples. This behavior could be explained assuming that another kind of clusters could exist in samples A and B. It also complies with the slowing down of critical fluctuations in the iron spin system. The temperature variation of both the intensity and linewidth of the EPR line of Fe^{3+} ions suggests that its origin is associated with a fraction of iron(III) ions, which at lower temperatures become ferromagnetically ordered and it is in agreement with the lower magnetic susceptibility.

Figs. 3a and 3b shows the temperature and frequency dependence of the dielectric constant (ϵ') and dielectric loss (ϵ'') for sample B, respectively. A peak of the dielectric constant is clearly observed around 210K, whose amplitude and position depend strongly on the frequency of the electric field.

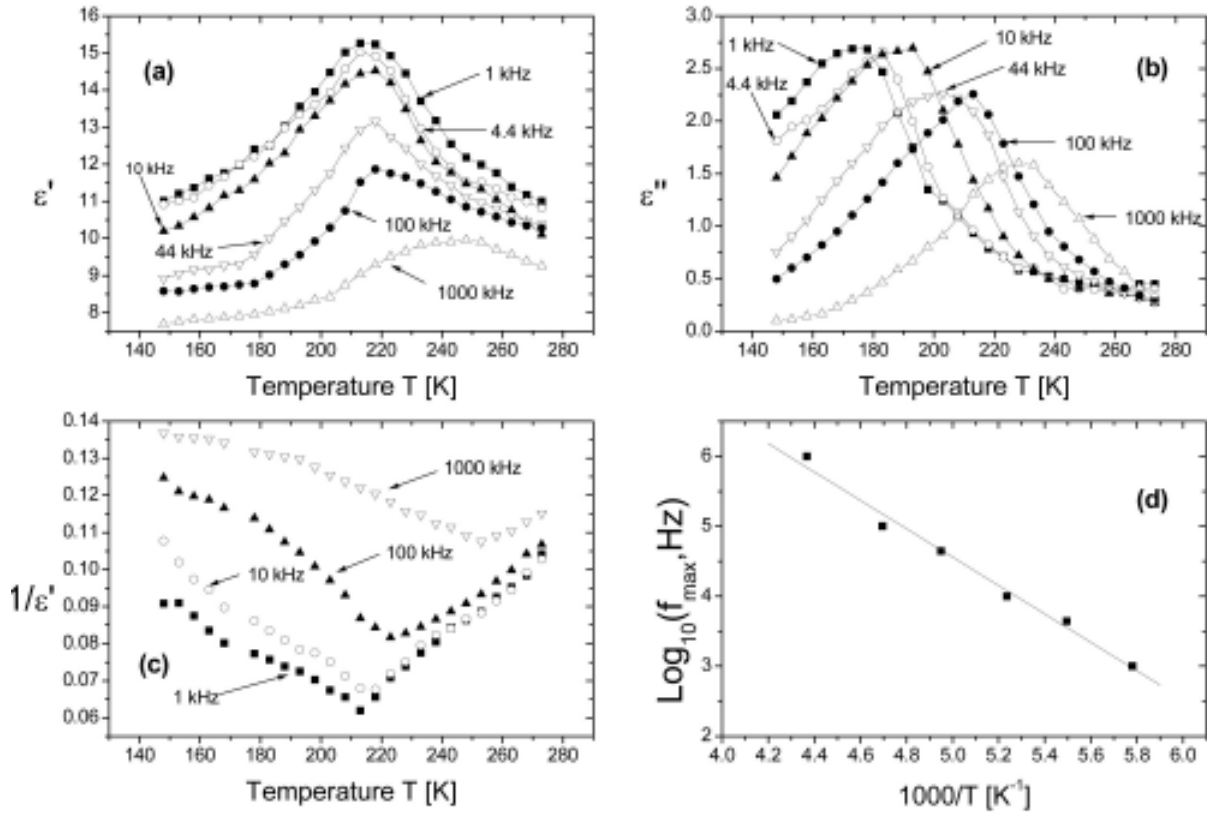


Fig. 3. Temperature dependence of the dielectric permittivity for sample B: (a) dielectric constant ϵ' , (b) dielectric loss ϵ'' , (c) reciprocal dielectric susceptibility $1/\epsilon'$, and (d) Arrhenius plot for ϵ'' .

In particular, the peak intensity decreases and shifts to higher temperatures with increasing frequency. The reciprocal dielectric susceptibility curves of $1/\epsilon'$ as a function of temperature for sample B are presented in Fig. 3c. The temperature dependence of the reciprocal dielectric susceptibility could be described with the Curie-Weiss law with constants $C_1 = -2326\text{K}$ and $C_2 = 1339\text{K}$. The ratio $|C_1/C_2| = 1.7$, which is close to 2 suggesting a weak second order phase transition from the paraelectric to ferroelectric state. Probably the dipole reorientation produces the ordering. We have suggested that the existence of clusters could explain this kind of temperature dependence of the dielectric susceptibility. Fig. 3b shows the variation with temperature of the imaginary part of the dielectric constant ϵ'' for sample B. The dielectric relaxation spectrum of as-received has one peak about 200K and varies with frequency. In addition there is the peak absorption, increasing with decreasing frequency, which inter-

feres with the lowest-frequency absorption at high temperatures. For each absorption, the temperature dependence of the frequency of maximum absorption is of the Arrhenius form $f_{\max} = f_0 \exp(-E_A/RT)$ where E_A is the activation energy. The plot of $\log_{10} f_{\max}$ is shown in Fig. 3d. The following value of activation energy is obtained $E_A = 0.42\text{ eV}$.

The magnetoelectric effect is well known and extensively studied for over 50 years, trying to find a correlation between magnetically and electrically ordered states [17,18]. A combination of the soft-mode theory for ferroelectric order and the molecular-field approximation for frustrated antiferromagnetic order has been used for the explanation of the thermodynamic properties of these systems [17]. Recently, an FMR study of magnetic nanoparticles embedded in a polymer matrix has shown a strong influence of the matrix relaxation on the position of the resonance line. The temperature gradient of the resonance field, dH_r/dT , has

increased over one order of magnitude during freezing of the matrix [19]. The anomalous behavior of the resonance field in a carbon matrix has suggested that "freezing" processes could be responsible for this kind of phenomena connected with magnetic ordering [20].

4. CONCLUSIONS

Two samples of the $Ni_2FeV_3O_{11-8}$ have been synthesized using two different annealing processes. The temperature dependence of the magnetic susceptibility has shown marked singularities which were assigned to the presence of different magnetic phases. Dielectric measurements have displayed a second order phase transition to the ferroelectric state at about 200K. Dielectric loss measurements have shown an intense peak at the same temperature and the activation energy of about 0.42 eV.

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REFERENCES

- [1] M.A. Lafontaine, J.M. Greneche, Y. Laligant and G. Ferey // *J. Solid State Chem.* **108** (1994) 1.
- [2] X. Wang, D. A. Vander Griend, C. L. Stern and K. P. Poeppelmeir // *J. Alloys Comp.* **298** (2000) 119.
- [3] N. Guskos, M. Wabia, M. Kurzawa, A. Bezkrvnyy, V. Likodimos, J. Typek, I. Rychlowska-Himmel and A. Blonska-Tabero // *Radiat. Eff. Defects Solids* **158** (2003) 369.
- [4] N. Guskos, J. Typek, A. Bezkrvnyy, M. Wabia, M. Kurzawa, E. A. Anagnostakis and G. Gasiorek // *J. Alloys Comp.* **377** (2004) 47.
- [5] N. Guskos, A. Bezkrvnyy, J. Typek, N. Yu. Ryabova, A. Blonska-Tabero, M. Kurzawa and M. Maryniak // *J. Alloys Comp.* **391** (2005) 20.
- [6] N. Guskos, A. Bezkrvnyy, J. Typek, N. Yu. Ryabova, A. Blonska-Tabero, M. Kurzawa and G. Zolnierkiwicz // *Materials Science-Poland* **23** (2005) 923.
- [7] G. Zolnierkiewicz, N. Guskos, J. Typek and A. Blonska-Tabero // *J. Non-Cryst. Solids* **352** (2006) 4362.
- [8] V. Likodimos, N. Guskos, S. Glenis, R. Szymczak, A. Bezkrvnyy, M. Wabia, J. Typek, G. Gasiorek, M. Kurzawa, I. Rychlowska-Himmel and A. Blonska-Tabero // *Eur. Phys. J. B* **38** (2004) 13.
- [9] N. Guskos, V. Likodimos, J. Typek, G. Zolnierkiewicz, R. Szymczak and A. Blonska-Tabero // *J. Non-Cryst. Solids* **352** (2006) 4179.
- [10] L. Kolpakowa, J. Pietrzak, J.N. Latosinska and P. Pawlicki // *J. Magn. Magn. Mater.* **140** (1995) 1583.
- [11] P. Pawlicki, L. Kolpakowa, A. Maryanowska, J. N. Latosinska and J. Pietrzak // *J. Magn. Magn. Mater.* **160** (1996) 372.
- [12] N. Guskos, V. Likodimos, S. Los, W. Kempinski, J. Stankowski, W. Wabia, J. Typek, A. Blonska-Tabero, P. Tabero and I. Rychlowska-Himmel // *Physica B* **284-288** (2000) 1456.
- [13] N. Guskos, J. Typek, G. Zolnierkiewicz, A. Blonska-Tabero, M. Kurzawa, S. Los and W. Kempinski // *Materials Science-Poland* **24** (2006) 985.
- [14] G. Zolnierkiewicz, N. Guskos, J. Typek and A. Blonska-Tabero // *Rev. Adv. Mater. Sci.* **12** (2006) 166.
- [15] M. Kurzawa, A. Blonska-Tabero, I. Rychlowska-Himmel and P. Tabero // *Mater. Res. Bull.* **36** (2001) 1379.
- [16] A.B. Melentev, L.L. Surat, A.A. Fotiev, G.A. Suvorova and T.P. Sirina // *Zh. Neorg. Khim.* **33** (1988) 2149.
- [17] C. Zhong and J. Fang // *Solid State Comm.* **128** (2003) 449.
- [18] Q. Jiang and S. J. Gong // *Eur. Phys. J. B* **43** (2005) 333.
- [19] N. Guskos, V. Likodimos, S. Glenis, J. Typek, M. Maryniak, Z. Roslaniec, M. Baran, R. Szymczak, D. Petridis and M. Kwiatkowska // *J. Appl. Phys.* **99** (2006) 084307.
- [20] G. Zolnierkiewicz, N. Guskos, J. Typek and A. Blonska-Tabero // *Acta Phys. Pol. A* **109** (2006) 675.