Current Topics in Biophysics 2010, 33 (suppl A), 277-281

MAGNETIC FRUSTRATION IN M-Fe-V-O SYSTEM

GRZEGORZ ZOLNIERKIEWICZ[1], NIKO GUSKOS[1,2], JANUSZ TYPEK[1]

[1]Institute of Physics, West Pomeranian University of Technology, Szczecin, Al. Piastow 48, 70-311 Szczecin, Poland
[2]Solid State Section, Department of Physics, University of Athens, Panepistimiopolis, 15 784 Zografou, Athens, Greece

Received June 7, 2010; accepted July 1, 2010; published online November 20, 2010.

Vanadium compounds from the M-Fe-V-O (M (II) = Zn (II), Mg (II), Cu (II), Mn (II) and Co (II)) system containing magnetic and nonmagnetic ions in the cationic sublattices exhibit structural randomness (iron ions could occupy different positions of ions M(II)). Oxygen deficiency observed in these compounds may be responsible for the emergence of competing magnetic interactions which prevent the formation of long-range magnetic order at high temperatures. Study of the temperature dependence of magnetic susceptibility and electron paramagnetic resonance (EPR) spectra of compounds from the M-Fe-V-O system has revealed the presence of significant spin frustration. It may be due to the Fe^{3+} ions located in cationic sublattices. Magnetic measurements of these systems showed the existence of strong antiferromagnetic interaction at high temperatures with high value of the Curie-Weiss temperature. Competing magnetic interactions allow to formation of long range magnetic order only at low temperatures. In particular, the static magnetic susceptibility for the $M_2FeV_3O_{11}$ (M(II)= Zn(II) and Mg(II)) compounds has revealed the existence of antiferromagnetic interaction between the Fe^{3+} spins with the Curie-Weiss temperature of θ = -55 K and the phase transition to a spin glass state at T_f = 2.5-2.8 K. Strong changes of the EPR parameters were observed at about 50 K. Similarly, in $M_3Fe_4V_6O_{24}$ compounds the high-temperature long-range magnetic order was not registered. For these compounds the Curie-Weiss temperature is high. Competition and frustration of magnetic processes may be responsible for the lack of long-range order at high temperatures despite the presence of a strongly coupled correlated spin system.

INTRODUCTION

Since the discovery of Kagome system ($M_3V_2O_8$ (M(II) = Cu(II), Ni(II) and Co(II)) with polyphase magnetic states the magnetic frustration phenomena have been intensively studied (Rogado *et al.* , 2003; Balakrishnan *et al.*, 2004; Lawes *et al.*, 2004; Lawes *et al.*, 2005; Szymczak *et al.*, 2006). The real microscopic quantum effect manifests itself by plateau and a step change in the temperature dependence of magnetization (Kageyama *et al.*, 1999; Matsuhira *et al.*, 2002; Moessner & Sondhi, 2003; Cabra *et al.*, 2002; Narumi *et al.*, 2004; Ono *et al.*, 2004; Hida, 2001; Zhitomirsky, 2002; Honecker *et al.*, 2004; Shnack *et al.*, 2001; Schulenburg *et al.*, 2002; Ramirez *et al.*, 2002; Richter *et al.*, 2004). These systems hold promise of new opportunities in practical applications (Zhitomirsky, 2003). These systems are in glass spin [Canals & Lacroix, 1998] or in frozen spin states (Ramirez *et al.*, 1999; Bramwell & Gingras, 2001). Measurements of the temperature dependence of the specific heat have showed the existence of phase transitions at temperatures of 6 and 11 K (Balakrishnan *et al.*, 2004).

Vanadium compounds in the M-Fe-V-O (M (II) = Zn (II), Mg (II), Cu (II), Mn (II) and Co (II)) system exhibit structural randomness in the cation sublattice as well as oxygen deficiency that play an important role in magnetic ordering processes at high temperatures (Guskos *et al.*, 2003; Guskos *et al.*, 2004). Trivalent iron ions in different sublattices (competing magnetic effects) may be responsible for the frustration of the spin system (Likodimos *et al.*, 2004; Guskos *et al.*, 2006a; Guskos *et al.*, 2007c). *Dc* magnetic susceptibility of $M_2FeV_3O_{11}$ (M(II) = Zn(II) and Mg(II)) compounds has showed the presence of a strong antiferromagnetic coupling with Curie-Weiss temperature, θ = -55 K, and the phase transition to spin glass state at T_f = 2.5-2.8 K (Lafontaine *et al.*, 1994; Wang *et al.*, 2000). These compounds are interesting in many applications (Zolnierkiewicz *et al.*, 2006; Binder & Young, 1986). Introduction of additional magnetic ions (eg $Ni_2FeV_3O_{11}$) may lead to more complicated magnetic structure (Guskos *et al.*, 2006b; Guskos *et al.*, 2007d). Thermogravimetric measurements of the $Zn_3Fe_4V_6O_{24}$ compound have suggested the existence of processes related to oxygen deficiency (Zolnierkiewicz *et al.*, 2008a; Zolnierkiewicz *et al.*, 2008b). Analysis of the EPR spectra of the $M_2InV_3O_{11}$ non-magnetic compounds (M (II) = Zn (II) and Mg (II)) showed that the spectra could be attributed to complexes involving vanadium ions at a low level of oxidation (Jaccarino & King, 1990). Antiferromagnets have geometrically frustrated spin-glass states and the random distribution of

magnetic fields (Belanger & Young, 1991; Ramirez *et al.*, 1994).

The aim of this report is to present our work on magnetic properties of compounds from the M-Fe-V-O system. They were studied by *dc* magnetization and magnetic resonance technique.

RESULTS AND DISCUSSION

Figures 1 and 2 present the crystallographic structure of the $Mn_3Fe_4V_6O_{24}$ compounds. It consists of two sublattices of iron ions and two sublattices of cation (magnetic or not magnetic). Disordering processes causing distribution of iron ions in a cationic sublattice are not so evident in these compounds as in $M_2FeV_3O_{11}$ (Guskos *et al.*, 2003; Guskos *et al.*, 2004; Guskos *et al.*, 2005; Bezkrovnyi *et al.*, 2005).

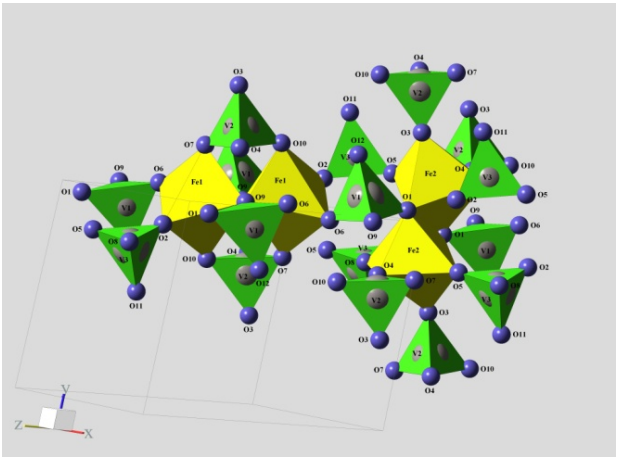

Fig. 1. Alignment of the iron Fe (1) and Fe (2) dimers, and their surrounding by vanadium tetrahedral.

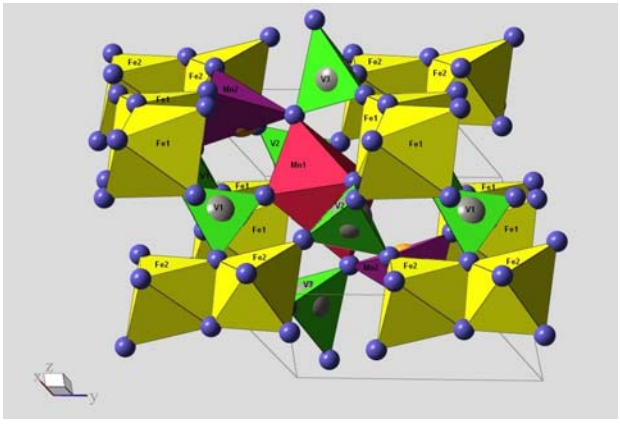

Fig. 2. Spatial arrangement of iron and manganese units in the $Mn_3Fe_4V_6O_{24}$ structure.

Figures 3 and 4 present the temperature dependence of magnetic susceptibility of the $Mg_3Fe_4V_6O_{24}$ compound [8]. The nature of the observed changes is similar in that a strong antiferromagnetic interaction with the Curie-Weiss temperature Θ=- 111 (1) K (and Θ=- 50 (1) K for $Mg_2FeV_3O_{11}$) is registered (Likodimos *et al.*, 2004; Guskos *et al.*, 2006a; Guskos *et al.*, 2007c). The long-range antiferromagnetic order is only observed at low temperatures (Fig. 4). Temperature dependence of $\chi^{-1}(T)$ is qualitatively similar for all compounds after the application of high magnetic field, what is particularly evident at low temperatures. This type of dependence is often observed in frustrated antiferromagnets, especially if diluted magnetic ions in the lattice are present. This implies the presence of antiferromagnetically correlated spin clusters and the relatively loose spins (Tobo *et al.*, 1996; Gorun & Lippard, 1991).

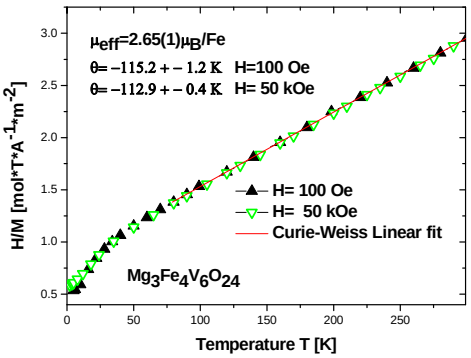

Fig. 3 Temperature dependence of inverse magnetic susceptibility, $\chi^{-1} = (M_{ZFC} / H)^{-1}$, for $Mg_3Fe_4V_6O_{24}$ at H = 100 Oe and 50 kOe. The solid lines are Curie-Weiss fits for high temperatures (T> 60 K) (Likodimos *et al.*, 2004; Guskos *et al.*, 2006a; Guskos *et al.*, 2007c).

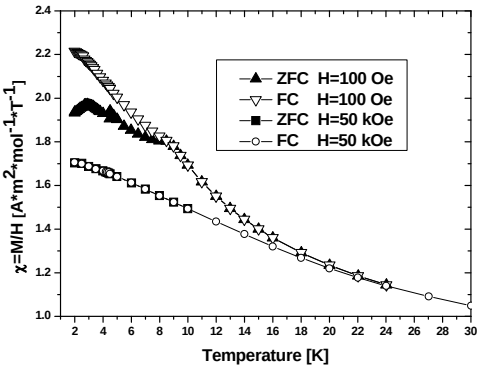

Fig. 4 Temperature dependence of ZFC and FC magnetization for two different values of magnetic fields for the $Mg_3Fe_4V_6O_{24}$ compound at low temperatures.

Figure 5 shows the observed EPR spectra for the $M_3Fe_4V_6O_{24}$ compounds at room temperature. The linewidth of the resonance line depends on the type of used ions. EPR line broadens with decreasing temperature, while decreases rapidly at low temperatures (for T< 30 K). At low temperatures, after disappearance of the main resonance line, many weak and narrow resonance lines appear, which are likely to come from other paramagnetic centres such as complexes of V(IV) ions (Zolnierkiewicz *et al.*, 2008a; Zolnierkiewicz *et al.*, 2008b) or Fe(III) at sites of low-symmetry of the crystal field. Analysis of lineshapes showed that lines can be properly fitted by Lorentzian function. Resonance absorption signal includes also contribution from the negative fields due to linearly polarized microwave field. This contribution has a significant effect when the linewidth is comparable with the resonance field. Distortion of the shape of the resonance line and its broadening suggests the long-range magnetic order at high temperatures.

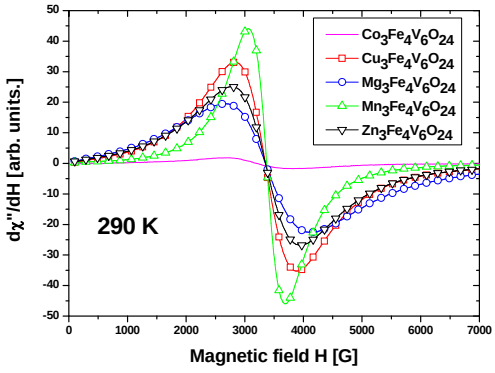

Fig. 5 EPR spectra of $M_3Fe_4V_6O_{24}$ (M(II)=Co(II), Cu(II), Mg(II), Mn(II) and Zn(II) compounds at high temperature.

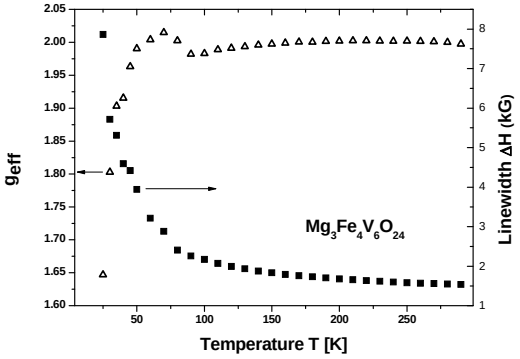

Fig. 6 Temperature dependence of g_{eff} (left axis) and linewidth ΔH_{pp} (right axis) for the $Mg_3Fe_4V_6O_{24}$ compound.

Figure 6 shows the temperature dependence of $g_{eff}(T)$ and the resonance linewidth $\Delta H_{pp}(T)$ obtained by fitting of the experimental spectrum by Lorentzian function. Significant change is observed for both parameters at temperatures below 80 K, and above T_1~ 8.5 K and T_2~ 3 K (Fig. 4). Broadening of the linewidth in the ($3<T/T_N<10$) temperature range observed often for AFM dielectrics is usually associated with the change of static magnetic susceptibility (Tobo *et al.*, 1996; Gorun & Lippard, 1991). Temperature dependence of the resonance linewidth $\Delta H_{pp}(T)$ can be represented by the following relationship: $\Delta H_{pp}(T)=[\chi_o(T)/\chi(T)]\Delta H_o$ where $\chi_o(T)=C/T$ is a free single-ion magnetic susceptibility, C is a Curie constant of the coupled paramagnetic system, while χ (T) is the static magnetic susceptibility and ΔH_o is temperature independent linewidth (at high temperatures) combined with a contribution from the anisotropic spin-spin interaction (Likodimos *et al.*, 2004; Guskos *et al.*, 2006a; Guskos *et al.*, 2007c). In this case, for $[\Delta H_{pp}(T)\chi_o(T)/\Delta H_o\chi(T)]$ a minimum at 90 K is observed, and there is correlation with a shift towards smaller fields of $g_{eff}(T)$ factor. Additionally, the temperature dependence of the product I·T shows a minimum at about 90 K (Fig. 7).

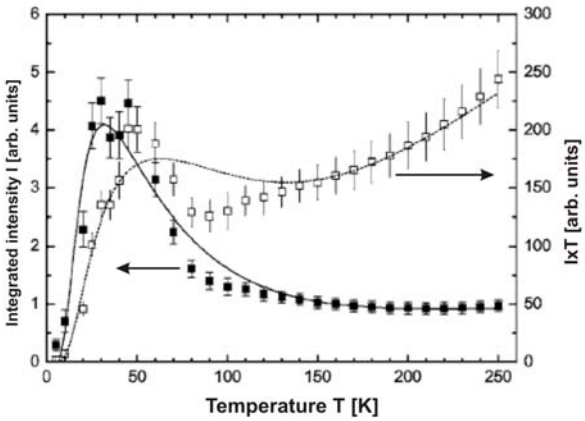

Fig. 7. Temperature dependence of the integrated intensity I(T) and the product I·T (right axis) for $Mg_3Fe_4V_6O_{24}$. Solid lines present the fitting for Fe(III)-F(III) dimer model (Likodimos *et al.*, 2004; Guskos *et al.*, 2006a; Guskos *et al.*, 2007c).

Measurements of *dc* magnetization and analysis of the EPR spectra in the $M_3Fe_4V_6O_{24}$ compounds have revealed the existence of significant magnetic frustration due to the loss of oxygen and non-equivalence of two magnetic sublattices. *Dc* magnetic susceptibility has showed that the spin freezing at low temperatures can be produced in two magnetic sublattices with T_f = 3K and 6K, and there is a strong correlation between the AFM spins at high temperatures. EPR studies showed the presence of AFM interactions and revealed the contribution of the magnetic ordering processes at around 230 K, although the static magnetization

measurements did not confirmed this finding. High frequency EPR (HF-EPR) measurements allowed to observe changes in the temperature dependence of g-factor and to compare it with its measurements at low frequency (X-band) EPR. Moreover, the use of HF-EPR can isolate the dominant type of magnetic interactions due to the application of very strong magnetic fields (Guskos *et al.*, 2009).

CONCLUSIONS

Structural and magnetic properties of M-Fe-V-O vanadium compounds have been investigated. The magnetic competition processes are responsible for the lack of long range magnetic order at high temperatures. At low temperatures the effects of spin frustration were observed. The disorder of magnetic ions in their sublattices and the oxygen deficiency could play a governing role in the magnetic competition phenomena.

ACKNOWLEDGMENTS

This research work was partially financed from Polish budget resources allocated to science in 2008-2010 as research project (0613/B/H03/2008/34).

REFERENCES

Balakrishnan G., Petrenko O. A., Lees M. R. & Paul D. M. K. (2004). Single crystals of the anisotropic Kagome staircase compounds $Ni_3V_2O_8$ and $Co_3V_2O_8$. *J. Phys.: Condens. Matter* **16**, L347 – L350.

Belanger D. P. & Young A. P. (1991). The random field Ising model. *J. Magn. Magn. Mater*. **100**, 272 – 291.

Bezkrovnyi A., Guskos N., Typek J., Ryabova N.Yu., Bosacka M., Blonska-Tabero A., Kurzawa M., Rychlowska-Himmel I. & Zolnierkiewicz G. (2005). Neutron diffraction study of $Mn_3Fe_4V_6O_{24}$. *Materials Science-Poland* **23**, 883 – 890.

Binder K. & Young A. P. (1986). Spin glasses: Experimental facts, theoretical concepts, and open questions. *Rev. Mod. Phys.* **58**, 801 – 976.

Bramwell S. T. & Gingras M. J. P. (2001). Spin ice state in frustrated magnetic pyrochlore. *Materials Science* **294**, 1495 – 1501.

Cabra D. C., Grynberg M. D., Holdsworth P. C. W. & Pujol P. (2002). From classical to quantum Kagomé antiferromagnet in a magnetic field. *Phys. Rev. B* **65**, 094418, 1 – 6.

Canals B. & Lacroix C. (1998). Pyrochlore antiferromagnet: a three-dimensional quantum spin liquid. *Phys. Rev. Lett.* **80**, 2933 – 2936.

Gorun S. M. & Lippard S. J. (1991). Magnetostructural correlations in magnetically coupled (.mu.-oxo)diiron(III) complexes. *Inorg. Chem.* **30**, 1625 – 1630.

Guskos N., Wabia M., Kurzawa M., Bezkrovnyj A., Typek J., Rychlowska-Himmel I. & Blonska-Tabero A. (2003). Neutron diffraction study of $Mg_2FeV_3O_{11-\delta}$. *Radiation Effects and Defects in Solids* **158**, 369 – 374.

Guskos N., Typek J., Bezkrovnyj A.., Likodimos V., Wabia M., Kurzawa M., Anagnostakis E.A. & Gasiorek G. (2004). Neutron studies of cation disorder in $Zn_2FeV_3O_{11-\delta}$. *J. All. Compd.* **377**, 47 – 52.

Guskos N., Bezkrovnjj A.., Typek J., Ryabova N.Yu.,. Blonska-Tabero A., Kurzawa M.& Maryniak M. (2005). Neutron diffraction study of $Zn_3Fe_4V_6O_{24}$. *J. All. Compd*. **391**, 20 – 25.

[a)]Guskos N., Likodimos V., Typek J., Zolnierkiewicz G. & Blonska-Tabero A. (2006). EPR study of disorder processes in the ternary vanadate $Zn_2FeV_3O_{11-x}$ compound. *J. Non-Cryst. Solids* **352**, 4250 – 4254.

[b)]Guskos N., Typek J., Zolnierkiewicz G., Blonska-Tabero A., Kurzawa M., Los S. & Kempinski W. (2006). Effects of thermal treatment on magnetic properties of $Ni_2FeV_3O_{11-\delta}$ compound. *Materials Science-Poland* **24,** 983 **–** 990.

[c)]Guskos N., Likodimos V., Glenis S., Zolnierkiewicz G., Typek J., Szymczak R. &. Blonska-Tabero A. (2007). Magnetic frustration in the site ordered $Mg_3Fe_4(VO_4)_6$ vanadate. *J. Appl. Phys.* **101**, 103922, 1 – 6.

[d)]Guskos N., Likodimos V., Glenis S., Typek J., Majszczyk J., Zolnierkiewicz G., Blonska-Tabero A. & Lin C.L. (2007). Magnetic and dielectric study of $Ni_2FeV_3O_{11-\delta}$. *Rev. Adv. Mat. Sci.* **14**, 85 – 89.

Guskos N., Ohta H., Zolnierkiewicz G., Okubo S., Zhang Wei-min, Typek J., Rudowicz C., Szymczak R., Bosacka M. & Nakamura T. (2009). Magnetic interactions in frustrated $Mn_3Fe_4(VO_4)_6$. *J. Non-Cryst. Solids* **355**, 1419 – 1426.

Hida K. (2001). Magnetization process of the *S*=1 and 1/2 uniform and distorted Kagomé Heisenberg antiferromagnets. *J. Phys. Soc. Jpn.* **70**, 3673 -3677.

Honecker A., Schulenburg J. & Richter J. (2004). Magnetization plateaus in frustrated antiferromagnetic quantum spin models. *J. Phys.: Condens. Matter* **16**, S749 – S758.

Jaccarino V. & King A. R. (1990). Random exchange and random field ising systems: Static and dynamic critical behavior. *Physica A* **163**, 291 – 305.

Kageyama H., Yoshimura K., Stern R., Mushnikov N. V., Onizuka K., Kato M., Kosuge K., Slichter C. P., Goto T. & Ueda Y. (1999). Exact dimer ground state and quantized magnetization plateaus in the two-dimensional spin system $SrCu_2(BO_3)_2$. *Phys. Rev. Lett.* **82**, 3168 – 3171.

Lafontaine M.A., Greneche J.M., Laligant Y. & Ferey G. (1994). β-$Cu_3Fe_4(VO_4)_6$: Structural study and relationships; physical properties. *J. Solid State Chem.*. **108**, 1 – 10.

Lawes G., Kenzelmann M., Rogado N., Kim K. H., Jorge G. A., Cava R. J., Aharony A., Entin-Wohlman O., Harris A. B., Yildirim T., Huang Q. Z., Park S., Broholm C. & Ramirez A. P. (2004). Competing magnetic phases on a Kagomé staircase. *Phys. Rev. Lett.* **93** 247201, 1 – 4.

Lawes G., Harris A.. B., Kimura T., Rogado N., Cava R. J., Aharony A., Entin-Wohlman O., Yildirim T., Kenzelmann M., Broholm C. & Ramirez A. P. (2005). Magnetically driven ferroelectric order in $Ni_3V_2O_8$. *Phys. Rev. Lett.* **95,** 087205, 1 – 4.

Likodimos V., Guskos N., Glenis S., Szymczak R., Bezkrovnyy A., Wabia M., Typek J., Gasiorek G., Kurzawa M., Rychlowska-Himmel I. & Blonska-Tabero A. (2004).

Magnetic properties of the antiferromagnetic site-disordered vanadate $Zn_2FeV_3O_{11}$. *Eur. Phys. J. B* **38**, 13 – 18.

Matsuhira K., Hiroi Z., Tayama T., Takagi S. & Sakakibara T. (2002). A new macroscopically degenerate ground state in the spin ice compound $Dy_2Ti_2O_7$ under a magnetic field. *J. Phys.: Condens. Matter* **14**, L559 – L565.

Moessner R. & Sondhi S. L. (2003). Theory of the [111] magnetization plateau in spin ice. *Phys. Rev. B* **68**, 064411, 1 – 12.

Narumi Y., Katsumata K., Honda Z., Domenge J.-C., Sindzingre P., Lhuillier C., Shimaoka Y., Kobayashi T. C. & Kindo K. (2004). Observation of a transient magnetization plateau in a quantum antiferromagnet on the Kagomé lattice. *Europhys. Lett.* **65**, 705 – 711.

Ono T., Tanaka H., Kolomiyets O., Mitamura H., Goto T., Nakajima K., Oosawa A., Koike Y., Kakurai K., Klenke J., Smeibidle P. & Meissner M. (2004). Magnetization plateaux of the S = 1/2 two-dimensional frustrated antiferromagnet Cs_2CuBr_4. *J. Phys.: Condens. Matter* **16**, S773 – S778.

Ramirez A. P. (1994). Strongly geometrically frustrated magnets. *Annu. Rev. Mater. Sci.* **24**, 453 – 480.

Ramirez A. P., Hayashi A., Cava R. J., Siddhartan R. & Shastry B. S. (1999). Zero-point entropy in 'spin ice'. *Nature (London)* **399**, 333 – 335.

Ramirez A. P., Shastry B. S., Hayashi A., Krajewski J. J., Huse D. A. & Cava R. J. (2002). Multiple field-induced phase transitions in the geometrically frustrated dipolar magnet: $Gd_2Ti_2O_7$. *Phys. Rev. Lett.* **89**, 067202, 1 – 4.

Richter J., Schulenburg J., Honecker A., Schnack J. & Schmidt H.-J. (2004). Exact eigenstates and macroscopic magnetization jumps in strongly frustrated spin lattices. *J. Phys.: Condens. Matter* **16**, S779 – S784.

Rogado N., Haas M. K., Lawes G., Huse D. A., Ramirez A. P. & Cava R. J. (2003). β-$Cu_3V_2O_8$: magnetic ordering in a spin-1/2 Kagomé-staircase lattice. *J. Phys.: Condens. Matter* **15**, 907 – 914.

Schnack J., Schmidt H.-J., Richter J. & Schulenburg J. (2001). Independent magnon states on magnetic polytopes. *Eur. Phys. J. B* **24**, 475 – 481.

Schulenburg J., Honecker A., Schnack J., Richter J. & Schmidt H.-J. (2002). Macroscopic magnetization jumps due to independent magnons in frustrated quantum spin lattices. *Phys. Rev. Lett.* **88**, 167207, 1 – 4.

Szymczak R., Baran M., Diduszko R., Fink-Finowski J., Gutowska M., Szewczyk A. & Szymczak H. (2006). Magnetic field-induced transitions in geometrically frustrated $Co_3V_2O_8$ single crystal. *Phys. Rev. B* **73,** 094425, 1 – 7.

Tobo A., Ito A. & Motoya K. (1996). Magnetic Property and Phase Diagram of the Diluted Antiferromagnet $Mn_xMg_{1-x}TiO_3$. *J. Phys. Soc. Japan* **65**, 2249 – 2258.

Wang X., Vander Griend D.A., Stern Ch.L. & Poeppelmeier K.R. (2000). Structure and cation distribution of new ternary vanadates $FeMg_2V_3O_{11}$ and $FeZn_2V_3O_{11}$. *J. Alloys Compd.* **298** 119 – 124.

Zhitomirsky M. E. (2002). Field-induced transitions in a Kagomé antiferromagnet. *Phys. Rev. Lett.* **88**, 057204, 1 – 4.

Zhitomirsky M. E. (2003). Enhanced magnetocaloric effect in frustrated magnets. *Phys. Rev. B* **67**, 104421, 1 – 7.

Zolnierkiewicz G., Guskos N., Typek J. & Blonska-Tabero A. (2006). EPR and TGA study of two $Zn_3Fe_4V_6O_{24-x}$ samples prepared by different thermal treatments. *J. Non-Cryst. Solids* **352**, 4362 – 4365.

[a)]Zolnierkiewicz G., Typek J.**,** Guskos N. & Bosacka M. (2008). EPR study of defect centers in new $Mg_2InV_3O_{11}$ vanadate. *Appl. Mag. Res.* **34**, 101 – 109.

[b)]Zolnierkiewicz G., Typek J.**,** Guskos N. & Bosacka M. (2008). EPR study of defect centers in $Zn_2InV_3O_{11}$. *J. Non-Cryst. Solids*. **354**, 4506 – 4509.