

# EPR study of phase formation in $\text{FeVO}_4\text{-Co}_3\text{V}_2\text{O}_8$ system



N. Guskos<sup>1,2</sup>, G. Zolnierkiewicz<sup>2</sup>, J. Typek<sup>2</sup>, and A. Blonska-Tabero<sup>3</sup>

<sup>1</sup>Solid State Physics, Department of Physics, University of Athens, Panepistimiopolis, 15 784 Zografos, Athens, Greece;

<sup>2</sup>Institute of Physics, West Pomeranian University of Technology, Al. Piastow 48, 70-311 Szczecin, Poland;

<sup>3</sup>Department of Inorganic and Analytical Chemistry, West Pomeranian University of Technology, Al. Piastow 42, 70-065 Szczecin, Poland.

## Abstract

Multicomponent vanadates  $\text{Co}_{3+x}\text{Fe}_{4-x}\text{V}_6\text{O}_{24}$  have been synthesized from an appropriate amount of  $\text{Co}_2\text{O}_3$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Fe}_2\text{O}_3$  metal oxides using the solid state reaction method. The electron paramagnetic resonance (EPR) spectra from twenty one samples representing different phases in the  $\text{FeVO}_4\text{-Co}_3\text{V}_2\text{O}_8$  system have been recorded at room temperature. The howardevansite structure (H-type phase) is formed which corresponds to the  $\text{Co}_{2.616}\text{Fe}_{4.256}\text{V}_6\text{O}_{24}$  compound while a homogeneity range of lyonsite (L-type phase) type structure could be described by the  $\text{Co}_{3+1.5x}\text{Fe}_{4-x}\text{V}_6\text{O}_{24}$  formula ( $0.476 < x < 1.667$ ). From samples in the system of L-type phase a very intense and broad symmetrical resonance line was recorded strongly depended on the phase relation in the  $\text{FeVO}_4\text{-Co}_3\text{V}_2\text{O}_8$  system. The system of H-type phase has shown a low intensity and narrow resonance signal.

## Introduction

Multicomponent vanadates  $\text{M}_3\text{Fe}_x\text{V}_6\text{O}_{24}$  ( $\text{M(II)}=\text{Cu(II), Zn(II), Mn(II) and Mg(II)}$ ) are very interesting from the point of view of their physical properties [1-5]. They could be formed in two different structural modifications. One of them was discovered in the summit crater fumaroles of the Izalco volcano in El Salvador (the  $\alpha\text{-Cu}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ , the mineral lyonsite) [1] and the other was synthesized in the laboratory  $\beta\text{-Cu}_3\text{Fe}_4\text{V}_6\text{O}_{24}$  phase which crystallizes as mineral howardevansite ( $\text{NaCuFe}_2\text{V}_3\text{O}_{12}$ ) [6]. The presence of isolated  $\text{VO}_4$  tetrahedron in their structure [1,3,6] could be very usefully in catalytic activity in the reactions of the oxidizing dehydrogenation of the saturated to unsaturated compounds [4,7]. The  $\text{FeVO}_4\text{-Co}_3\text{V}_2\text{O}_8$  system containing two strong magnetic ions seems suitable for investigation of formation of the lyonsite and howardevansite phases [8]. The study of magnetic properties of multicomponent vanadates  $\text{M}_3\text{Fe}_x\text{V}_6\text{O}_{24}$  ( $\text{M(II)}=\text{Zn(II), Mg(II) and Mn(II)}$ ) has shown the presence of strongly coupled magnetic processes [3]. The EPR measurements suggested that the magnetically ordered states could appear in the high temperature range but the temperature dependence of magnetic susceptibility indicated that this process could be acting at very low temperature. This controversy could be explained by assuming competition of magnetic interactions [3]. One of the interesting problems still to be solved in studying the  $\text{M}_3\text{FeV}_3\text{O}_{11}$  and  $\text{M}_3\text{Fe}_x\text{V}_6\text{O}_{24}$  systems is that there is no EPR signal in samples containing  $\text{M(II)}=\text{Co(II)}$ . Up to now the crystal structure of  $\text{Ni}_3\text{FeV}_3\text{O}_{11}$  is still unresolved and complicated magnetic interactions causes formation of short-range ordered areas which produce the ferromagnetic resonance signal [9]. The phase formation in the  $\text{FeVO}_4\text{-Co}_3\text{V}_2\text{O}_8$  system in the whole range of components and determination of the range of homogeneity of the phases of lyonsite and howardevansite type structures could be helped by EPR study of these materials. Two strong magnetic ions - cobalt and iron - could be responsible for formation of magnetic agglomerates which could add additional information, improving understanding of their unusually polymorphic modifications.

The aim of this report is to study by the EPR method of twenty one samples formed in the  $\text{FeVO}_4\text{-Co}_3\text{V}_2\text{O}_8$  system. The annealing process and concentration procedure is used for the analysis of EPR spectra and particular attention is paid in searching for magnetic agglomerates with their magnetic interaction by introduction of magnetic ions (cobalt and iron) in the sublattice.

Sample	Resonance field $H_r$ [Gs]	$g_{\text{eff}}$	Linewidth $\Delta H_{\text{pp}}$ [Gs]	Integrated Intensity $I \Delta H_{\text{pp}}^2$	Heating conditions
1**	3428.1(3)	1.960(1)	1565(1)	$4.5 \cdot 10^3$	680°C(20h)+2x780°C
3*	3429.3(3)	1.959(1)	1565(1)	$4.9 \cdot 10^3$	580°C+ 680°C +720°C+3x800°C
4*	3330.0(3)	2.018(1)	1570(1)	$4.0 \cdot 10^2$	570°C+680°C+720°C+740°C +790°C+800°C
5*	3388.1(3)	1.983(1)	1786(1)	$1.3 \cdot 10^3$	570°C+675°C+800°C
6**	3218.4(3)	2.088(1)	1276(1)	$2.1 \cdot 10^2$	670°C+690°C+3x740°C+780°C
8**	3218.3(3)	2.088(1)	1510(1)	$3.6 \cdot 10^2$	700°C+780°C+800°C+820°C+840°C
9*	3127.0(3)	2.149(1)	1254(1)	$5.6 \cdot 10^2$	560°C+600°C+675°C+800°C+2x840°C
10*	3000.4(3)	2.240(1)	1220(1)	$1.5 \cdot 10^2$	560°C+600°C+610°C+675°C+700°C +750°C+2x840°C
13*	No EPR signal				560°C+600°C+680°C+830°C+910°C
14*	2875.0(3)	2.337(1)	300(1)	1.1·10	580°C+680°C+2x720°C+2x920°C
15*	3415.0(3)	1.968(1)	96(1)	1.0	570°C+620°C+730°C+2x920°C
16*	2901.2(3)	2.316(1)	230(1)	5.0	570°C+2x600°C+700°C+2x920°C
18*	No EPR signal				560°C+600°C+680°C+830°C+910°C
19*	2907.0(3)	2.312(1)	166(1)	4.2	575°C+2x600°C+2x920°C
20*	2919.0(3)	2.302(1)	150(1)	1.6	570°C+2x600°C+700°C+2x920°C
21**	No EPR signal				680°C+2x930°C
22*	2580.0(3)	2.605(1)	380(1)	1.4·10	570°C+3x600°C+700°C+2x920°C
23**	2764.0(3)	2.431(1)	2520(1)	$2.9 \cdot 10^3$	680°C+930°C+920°C
24**	2871.0(3)	2.341(1)	2550(1)	$4.0 \cdot 10^3$	680°C+680°C+930°C+920°C

\*Synthesized from three components:  $\text{CoCO}_3+\text{V}_2\text{O}_5+\text{Fe}_2\text{O}_3$

\*\*Synthesized from two components:  $\text{Co}_3\text{V}_2\text{O}_8+\text{FeVO}_4$

Table 1. The EPR parameters of the samples from the  $\text{FeVO}_4\text{-Co}_3\text{V}_2\text{O}_8$  system (Sample numbering according to A. Blonska-Tabero and M. Kurzawa, *J. Therm. Anal. Calor.* **88**, 33 (2007).

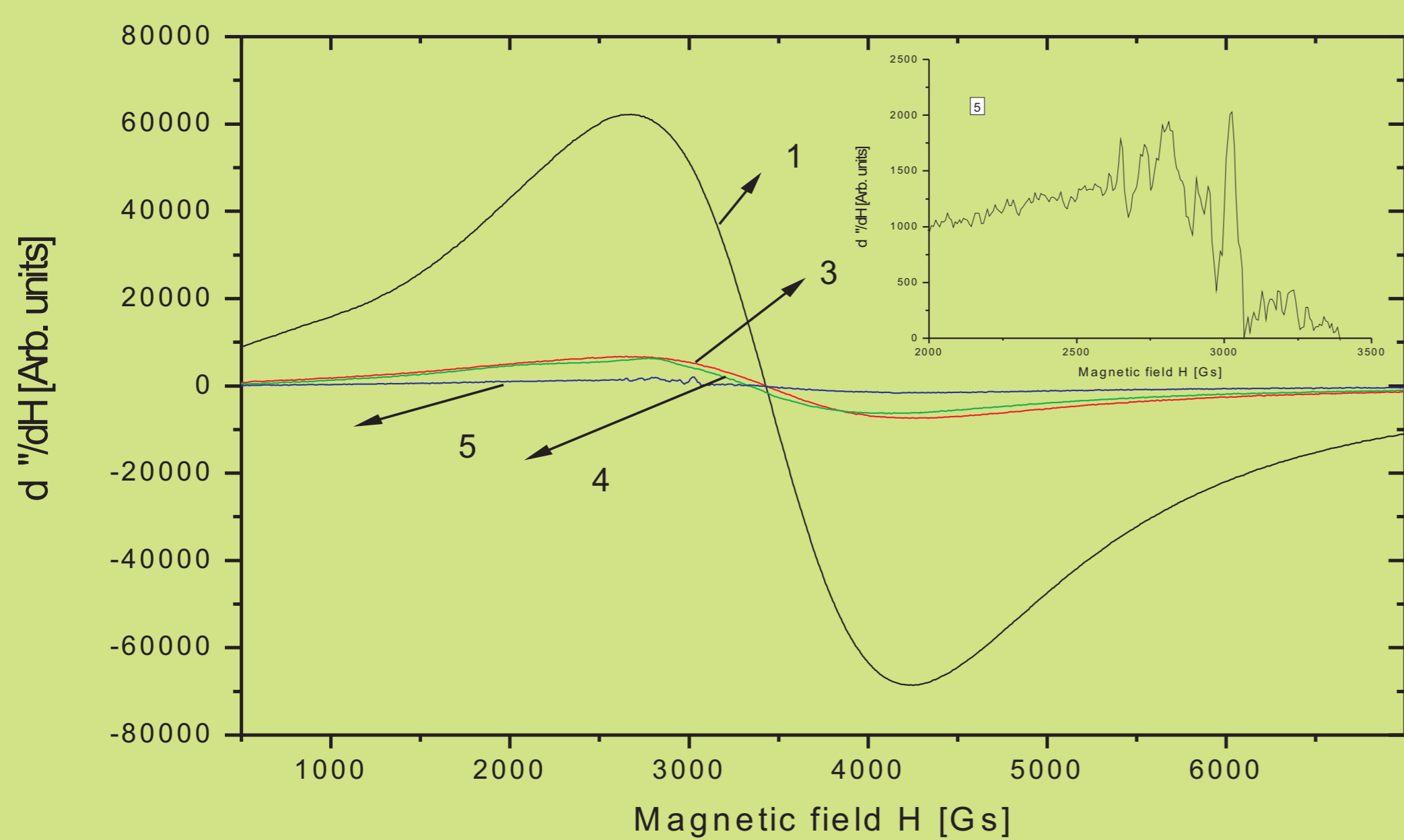


Figure 1 The EPR spectra of samples from the  $\text{FeVO}_4\text{-Co}_3\text{V}_2\text{O}_8$  system.

