EPR STUDY OF THE $Me_2InV_3O_{11-\delta}$ (Me = Mg, Zn) COMPOUNDS

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Abstract. Two new compounds from the multicomponent vanadates $Me_2InV_3O_{11-\delta}$ (Me=Mg, Zn) have been synthesized and investigated by electron paramagnetic resonance (EPR) at room temperature. XRD measurements have shown that they are isostructural with the magnetic system $Me_2FeV_3O_{11-\delta}$. The EPR spectra of the $Mg_2InV_3O_{11-\delta}$ and $Zn_2InV_3O_{11-\delta}$ compounds originated from defect centers consisting of V(IV) ions and clusters. For $Mg_2InV_3O_{11-\delta}$ the EPR spectrum with hyperfine structure was observed with the following spin Hamiltonian parameters: $g_{\parallel} = 1.93$, $g_{\perp} = 1.94$ and $A_{\parallel} = 180 \cdot 10^{-4}$ cm^{-1}, $A_{\perp} = 50 \cdot 10^{-4}$ cm^{-1}. A weak line attributed to the forbidden $\Delta M_S = \pm 2$ transition was registered at low magnetic field of 163 mT. For the $Zn_2InV_3O_{11-\delta}$ compound two resonance lines were observed; one centered at g=1.967(3) with linewidth ΔH=4.8(9) mT and another at g=2.82(1) with ΔH=28(1) mT. The appearance of the EPR spectra was correlated with oxygen deficiency phenomena playing an active role in determining the magnetic properties of these compounds.

1. INTRODUCTION

The multicomponent vanadates of the $Me_2BV_3O_{11-\delta}$ type (where Me is metal ion and B=Fe, In, Cr) form a very complicated structural system with exceptionally interesting physical properties [1-7]. In the Me-Fe-V-O system iron(III) ions are disordered in the cation positions and vanadium ions, due to oxygen deficiency, appear in different valence states. This generates competition of the magnetic interactions, leading to magnetic frustration [7,8]. The temperature dependence of the EPR spectra of compounds from this system have shown that magnetic ordering processes are active in the high temperature range (T>200K), but neutron diffraction studies down to 11K have not recorded any magnetically ordered state [5-9]. The stabilization of the physical properties of compounds from the multicomponent vanadate system is very difficult because slight temperature changes in the annealing processes during their syntheses could have substantial effects, as shown by TGA measurements [10]. The valence state of vanadium ions is especially important as it is easily influenced by oxidation. In this context it is desirable to study compounds from the Me-B-V-O system in which B and Me are nonmagnetic ions as it may reveal the magnetic interactions of vanadium ions.

The aim of this paper is to report the study of the EPR spectra in the multicomponent vanadates $Me_2InV_3O_{11-\delta}$ (Me = Zn, Mg) and to analyze the

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Table 1. Lattice parameters for compounds from the $Me_2BV_3O_{11}$ system [5,8,18].

Parameter	$Mg_2FeV_3O_{11}$ [1]	$Zn_2FeV_3O_{11}$ [2]	$Mg_2InV_3O_{11}$ [18]	$Zn_2InV_3O_{11}$ [18]
a [Å]	6.4437(9)	6.4538(5)	6.434(1)	6.346(1)
b [Å]	6.8146(9)	6.8393(4)	6.830(1)	6.729(1)
c [Å]	10.109(1)	9.9924(7)	10.174(1)	10.187(1)
α [°]	97.35(1)	97.556(9)	97.0(1)	96.2(1)
β [°]	103.45(1)	102.650(8)	103.2(1)	104.0(1)
γ [°]	101.51(1)	101.308(8)	100.6(1)	94.2(1)
V [Å³]	415.91	414.92	421.53	417.43
ρ_{calc} [g·cm⁻³]	3.479	4.129	3.88(5)	4.48(5)

magnetic properties of these compounds determined by vanadium ions.

2. EXPERIMENTAL

Polycrystalline multicomponent vanadates of the $Me_2InV_3O_{11-\delta}$ (Me=Zn, Mg) type were obtained by a solid-state reaction method from a stoichiometric mixture of the V_2O_5, In_2O_3, $3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$, and ZnO oxides [11]. The samples were repetitively ground, pressed into pellets and calcinated in air at 540 °C for 24 hrs and then at 640 °C for 24 hrs. At each heating stage the samples were slowly cooled to room temperature, ground and analyzed by differential thermal analysis and X-ray diffraction (XRD), until the formation of a single phase sample could be verified. The diffraction patterns were obtained with a Philips type (X" Pert PRO) X-ray diffractometer using the CoK_α radiation and an iron filter.

The EPR spectra were recorded using a standard X-band spectrometer type Bruker E 500 (ν=9.5 GHz) with magnetic field modulation of 100 kHz. The magnetic field was scaled with a NMR magnetometer. The samples, containing 20 mg of the substance in the form of fine powder, without any cement-dielectric, were sealed into 5 mm in diameter quartz tubes. The EPR measurements were done at room temperature.

3. RESULTS AND DISCUSSION

X-ray structural determination of the multicomponent vanadate $Me_2InV_3O_{11-\delta}$ (Me=Zn and Mg) showed that both compounds are isostructural to $Zn_2GaV_3O_{11-\delta}$ [2], crystallizing in the triclinic space group P–1 (Z=1) [4]. The obtained lattice parameters for the $Zn_2InV_3O_{11-\delta}$ and $Mg_2InV_3O_{11-\delta}$ compounds are given in Table 1 and they are compared with similar compounds in which indium(III) ions are replaced by iron(III) ions. The $Mg_2InV_3O_{11-\delta}$ and $Zn_2InV_3O_{11-\delta}$ compounds differ slightly in values of the lattice parameters in comparison to their iron (III) counterparts: $\Delta a = a_{Fe} - a_{In} = 0.0097$ Å, $\Delta b = b_{Fe} - b_{In} = -0.0154$ Å, $\Delta c = c_{Fe} - c_{In} = -0.065$ Å for $Mg_2InV_3O_{11-\delta}$, and $\Delta a = a_{Fe} - a_{In} = 0.1078$ Å, $\Delta b = b_{Fe} - b_{In} = 0.1103$ Å, $\Delta c = c_{Fe} - c_{In} = -0.1949$ Å for $Zn_2InV_3O_{11-\delta}$. The largest difference in lattice parameters is observed for the c-axis. The volume of the unit cell is greater for compounds with indium(III) ions what is caused by the larger ionic radius of that ion (0.80 Å in 6-fold coordination) in comparison with iron(III) ion (0.645 Å in 6-fold coordination).

Figs. 1 and 2 present the EPR spectra of the $Mg_2InV_3O_{11-\delta}$ and $Zn_2InV_3O_{11-\delta}$ compounds at room temperature. Surprisingly, there are easily observed differences between these two spectra. The EPR spectrum of $Mg_2InV_3O_{11-\delta}$ compound (Fig. 1) is composed of at least two spectral components: a broad line centered at g_{eff} ~2 without any structure and a well resolved hyperfine spectrum (HFS) typical of isolated vanadium ions in axial symmetry, present as VO^{2+} species similar as in $SbVO_5$ [12]. Additionally, in both samples at low magnetic fields a spectral component centered at g_{eff} ~4 is visible. It is usually attributed to the presence of vanadium dimeric species and to the forbidden $\Delta M_S = \pm 2$ transitions. The broad EPR line without fine structure could be recognized as originating from a mobile electron hopping along the V^{4+}-O-V^{5+} bond [13]. The
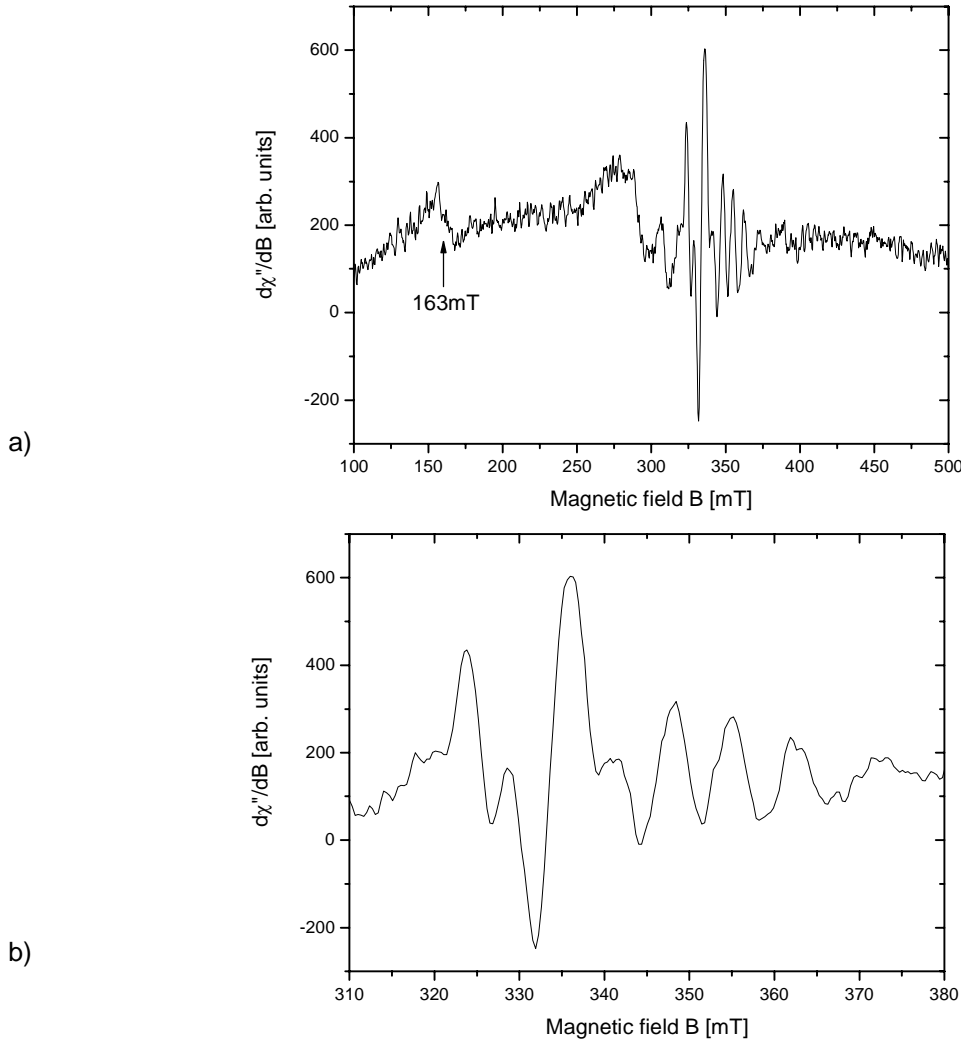
Fig. 1. EPR spectrum of the Mg$_2$InV$_3$O$_{11-\delta}$ compound at room temperature (a), expanded view around the γ~2 spectral range (b).

EPR of Zn$_2$InV$_3$O$_{11-\delta}$ compound consists of three types of lines: a narrow one centered at g_{eff} =1.967(3) with linewidth ΔH=4.8(9) mT, a broad line similar to Mg$_2$InV$_3$O$_{11-\delta}$ and another spectral feature at g_{eff} =2.82(1) with ΔH=28(1) mT (Fig. 2). The narrow line is similar to the one observed in non-stoichiometric compounds in vanadium oxide [14]. The broad line appearing at low magnetic fields could arise from ferromagnetically coupled clusters of vanadium ions [15].

The EPR spectra due to the interaction of the electron spin (S=1/2) with the ^{51}V nucleus (I=7/2, abundance 99.75%) could be described by an axial spin-Hamiltonian of the form:

$$H = \mu_B[g_{\parallel}B_zS_z + g_{\perp}(B_xS_x + B_yS_y)] + A_{\parallel}S_zI_z + A_{\perp}(S_xI_x + S_yI_y), \quad (1)$$

where μ_B is the Bohr magneton; $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}$, $A_{\perp}$ are the spin-Hamiltonian parameters, B_x, B_y, B_z are the components of the magnetic field; S_x, S_y, S_z and I_z, I_x, I_y are the components of the spin operators of electron and nucleus, respectively. The hyperfine parameters can be calculated by the following relations [16]:

$$B_{\parallel}(m)=B_{\parallel}(0) - mA_{\parallel} - A_{\perp}^2(63/4 - m^2)/2B_{\parallel}(0), \quad (2)$$

$$B_{\perp}(m) = B_{\perp}(0) - mA_{\perp} - (A_{\parallel}^2 + A_{\perp}^2)(63/4 - m^2)/4B_{\perp}(0), \quad (3)$$
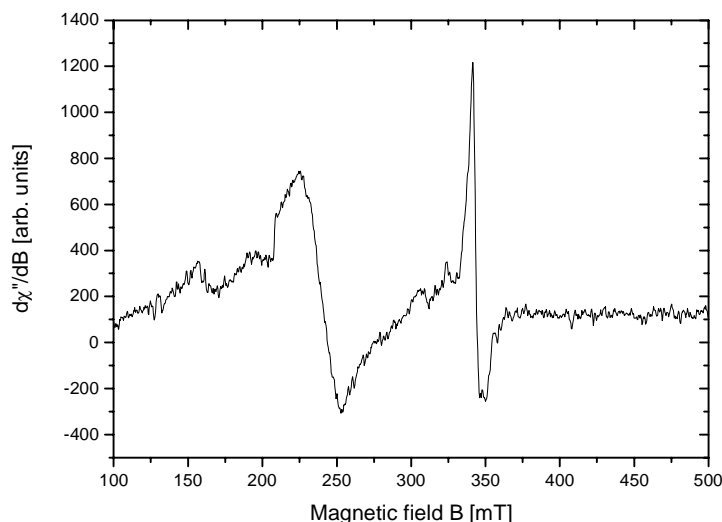
Fig. 2. EPR spectrum of the $Zn_2InV_3O_{11-\delta}$ compound at room temperature.

where $B_\parallel(0)=h\nu/g_\parallel\mu_B$, $B_\perp(0)=h\nu/g_\perp\mu_B$, and m is the nuclear magnetic quantum number. The spin-Hamiltonian parameters were calculated using the procedure described in [17]. The g and A values obtained from the EPR spectrum of the $Mg_2InV_3O_{11-d}$ compound are as follows: $g_\parallel = 1.93$, $g_\perp = 1.94$ and $A_\parallel = 180\cdot10^{-4}$ cm^{-1}, $A_\perp = 50\cdot10^{-4}$ cm^{-1}.

Vanadium ions exhibit a wide range of stable oxidation states, among them frequently encountered are the V(IV) and V(V) states. Vanadium(V) ion, with a $3d^0$ configuration, is diamagnetic and thus EPR inactive. Vanadium(IV) clusters give rise to a broad signal owing to significant dipolar interactions, whereas isolated V(IV) species exhibit a hyperfine structure derived from the interaction of the $3d^1$ electron with the magnetic nuclear moment of ^{51}V. In solids, the hyperfine structure can be substantially suppressed or even disappear completely due to various interactions of electron spins with their surroundings. The nominal oxidation state of bulk vanadium ions in $Mg_2InV_3O_{11}$ compounds is +5. Comparison with a $CuSO_4$ reference sample allowed estimating that only 0.2% of all vanadium ions in the investigated compounds is EPR active. The existence of even that small number of paramagnetic vanadium ions could have significant influence on the physical properties of the multicomponent vanadate oxide system [9]. The number of V(IV) paramagnetic ions in the $Me_2InV_3O_{11}$ compounds is strongly dependent on the high-temperature annealing and thus on the oxygen deficiency processes. Heating of $Me_2InV_3O_{11}$ samples causes conversion of V(V) to V(IV) and the loss of oxygen. As the electrons needed for vanadium conversion originate from released oxygen, the bigger the oxygen loss the stronger the intensity of the EPR signal. Thus the presence of paramagnetic centres registered by the EPR spectroscopy might be the indicator of the strength of oxygen deficiency occurring in these compounds.

In conclusion, two multicomponent vanadates $Me_2InV_3O_{11-\delta}$ (Me=Zn and Mg) have been synthesized and studied by EPR spectroscopy. The EPR spectra originated from paramagnetic defect centers involving V(IV) ions and clusters. The presence of such centers is correlated with the oxygen deficiency processes registered previously for these compounds.

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