

## MAGNETIC RESONANCE STUDY OF PHASES FROM Sb-V-O AND Sb-V-Mo-O SYSTEMS

JANUSZ TYPEK<sup>1</sup>, ELŻBIETA FILIPEK<sup>2</sup>, NIKO GUSKOS<sup>1</sup>

<sup>1</sup>Institute of Physics, West Pomeranian University of Technology, 70-311 Szczecin, Al. Piastow 48, Poland

<sup>2</sup>Department of Inorganic and Analytical Chemistry, West Pomeranian University of Technology, 71-065 Szczecin, Al. Piastow 42, Poland

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Electron paramagnetic resonance (EPR) study of selected phases formed in the Sb-V-O and Sb-V-Mo-O systems has been carried out in the 3-300 K temperature range. The following compounds were investigated:  $\text{SbVO}_5$ ,  $\text{Sb}_3\text{V}_2\text{Mo}_3\text{O}_{21}$ , and six samples containing phase type solid solutions of  $\text{MoO}_3$  in  $\text{SbVO}_5$ . As the catalytic activity of these materials depends crucially on the concentration and type of defect center, EPR technique will be used to provide this important information. In powder samples of  $\text{SbVO}_5$  three kinds of paramagnetic defect centers involving vanadium ions were found: one center involving a mobile electron hopping along a  $\text{V}^{4+}\text{-O-V}^{5+}$  bond producing a broad EPR line without hyperfine structure, the second centre is formed by  $\text{VO}^{2+}$  ions in octahedral coordination with a tetragonal compression, and the third complex is a dimer composed of two interacting  $\text{VO}^{2+}$  ions. Study of thermal decomposition products of  $\text{SbVO}_5$  revealed in EPR spectrum a broad component arising from vanadium(IV) clusters present inside the micrograins forming powder sample, and a narrow component due to vanadium(IV) ions located on the surface of these grains. EPR spectra of  $\text{Sb}_3\text{V}_2\text{Mo}_3\text{O}_{21}$  registered in the 4-290 K temperature range represent a very broad line that has been decomposed on three anisotropic components. The temperature dependence of these components has been studied revealing a strong change of that component connected with the z axis of vanadium cluster. Only 11.3% of all vanadium ions in  $\text{Sb}_3\text{V}_2\text{Mo}_3\text{O}_{21}$  are magnetic and could be revealed by EPR method. In the case of  $\text{SbVO}_5\text{:MoO}_3$  solid solutions the problem of charge compensation could be resolved by EPR study. The dominating mechanism of compensation of an excessive charge of  $\text{Mo}^{6+}$  ion is realized by cation vacancy formation, although a significant part (~25%) of  $\text{Mo}^{6+}$  ions takes part in valence state reduction of  $\text{V}^{5+}$  ions.

### INTRODUCTION

Compounds forming in the  $\text{V}_2\text{O}_5\text{-Sb}_2\text{O}_4$  (V-Sb-O) and  $\text{V}_2\text{O}_5\text{-MoO}_3\text{-Sb}_2\text{O}_4$  (V-Sb-Mo-O) oxides systems in air atmosphere are well known as potential components of catalysts having a good selectivity and activity in oxidation of isobutene to methacroleine, in ammoxidation of propane to acrylonitrile and are used in production of maleic anhydride and formaldehyde (Grasseli, 1999). In this paper the following compounds will be studied:  $\text{SbVO}_5$ ,  $\text{Sb}_3\text{V}_2\text{Mo}_3\text{O}_{21}$  and six different samples of  $\text{MoO}_3$  solid solutions in  $\text{SbVO}_5$ . They are all shown on the component concentration triangle of the  $\text{Sb}_2\text{O}_4\text{-V}_2\text{O}_5\text{-MoO}_3$  system in Fig. 1.

Electron paramagnetic resonance (EPR) is a valuable and sensitive technique to find out the presence of paramagnetic centers, to deduce their local symmetry and to infer the type of magnetic interactions they are involved. In case of compounds containing paramagnetic ions from the iron group the usage of EPR method helped address important questions of practical importance (Typek, Guskos & Filipek, 2008; Typek, Guskos, Filipek & Piz, 2010).

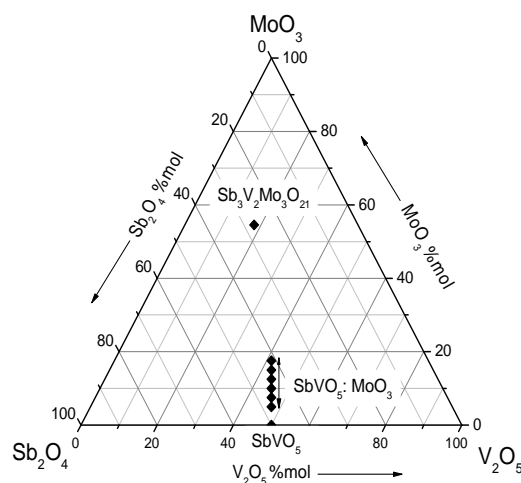


Fig.1. Location of the investigated samples on the component concentration triangle of the  $\text{Sb}_2\text{O}_4\text{-V}_2\text{O}_5\text{-MoO}_3$  system.

For compounds from the  $\text{V}_2\text{O}_5\text{-MoO}_3\text{-Sb}_2\text{O}_4$  system the oxidation state of vanadium ions and the structure of

paramagnetic centers are of primary importance.

These questions will be tackled by registration of EPR spectra of the studied materials in a wide temperature range.

## EXPERIMENTAL

All investigated samples were synthesized by solid state reaction method.

Samples of  $\text{SbVO}_5$  were produced by heating in air equimolar mixture of  $\text{V}_2\text{O}_5$  with  $\alpha\text{-Sb}_2\text{O}_4$  in the following stages: stage I:  $550^\circ\text{C} \rightarrow 600^\circ\text{C}$  (48h), stage II:  $600^\circ\text{C} \rightarrow 600^\circ\text{C}$  (48h); stage III:  $600^\circ\text{C} \rightarrow 620^\circ\text{C}$  (24h); stage IV:  $620^\circ\text{C} \rightarrow 650^\circ\text{C}$  (48h); stage V:  $650^\circ\text{C} \rightarrow 650^\circ\text{C}$  (48h) (Filipek, 1999).

Samples of  $\text{Sb}_3\text{V}_2\text{Mo}_3\text{O}_{21}$  were obtained from mixture of  $\text{V}_2\text{O}_5$ ,  $\text{MoO}_3$  and  $\alpha\text{-Sb}_2\text{O}_4$  in 2:6:3 molar ratio, respectively. The mixture was heated in the following stages: stage I:  $400^\circ\text{C}$  (1h)  $\rightarrow 500^\circ\text{C}$  (8h)  $\rightarrow 550^\circ\text{C}$  (24h); stage II:  $575^\circ\text{C}$  (24h); stage III:  $600^\circ\text{C}$  (24h); stage IV:  $625^\circ\text{C}$ ; stage V:  $650^\circ\text{C}$  (48h) (Filipek, 2001).

Samples of  $\text{MoO}_3$  solid solutions in  $\text{SbVO}_5$  were made by homogenization of the reagents in suitable proportions by grinding, shaped into pastilles and then heated in the following stages: stage I  $400^\circ\text{C}$  (1h)  $\rightarrow 500^\circ\text{C}$  (24h)  $\rightarrow 500^\circ\text{C}$  (24h); stage II:  $600^\circ\text{C}$  (48h); stage III:  $630^\circ\text{C}$  (24h); stage IV:  $645^\circ\text{C}$  (24h). After each heating stage samples cooled in the furnace to room temperature were weighted to check mass change, homogenized by grinding and their composition was determined by XRD analysis (DRON-3 diffractometer, radiation  $\text{CoK}\alpha$ , filter Fe) (Filipek, 2006). The following  $\text{SbVO}_5:(\text{MoO}_3)_z$  solid solutions were studied:  $z=5.0, 7.5, 10.0, 12.5, 15.0, 17.5$ , were  $z$  is  $\text{MoO}_3$  %mol in the initial mixture.

The EPR experiments were performed on a BRUKER E500 spectrometer operating at X-band microwave frequency equipped with  $\text{TE}_{102}$  cavity with 100 kHz field modulation. The temperature variation studies in the range of 3.6-300 K were performed using an Oxford ESP 300 continuous-flow cryostat.

## RESULTS AND DISCUSSION

### A. $\text{SbVO}_5$

The presence of three types of paramagnetic centres has been identified in  $\text{SbVO}_5$  (Typek, Guskos, Buchowski, Wabia & Filipek, 2002). All are connected with the defect centres, which could have a significant influence, e.g. on the electrical and transport properties of this material. Only a very weak EPR signal from sample of  $\text{SbVO}_5$  was detected at room temperature. Comparison of the spectrum with the  $\text{CuSO}_4$  reference sample allowed to estimate the number of paramagnetic

centers involved in the resonance phenomenon. The obtained value of 0.02% EPR active ions of the total vanadium ions certifies that there are no bulk  $\text{V}^{4+}$  ions in  $\text{SbVO}_5$  structure.

EPR spectra obtained in the low temperature range, below 100 K, are presented in Fig. 2. They could be regarded as composed of two components: a broad signal in the range of  $g \sim 2$  without hyperfine structure (hfs) and a well resolved hfs lines typical of isolated vanadium ions in axial symmetry, present as  $\text{VO}^{2+}$  species.

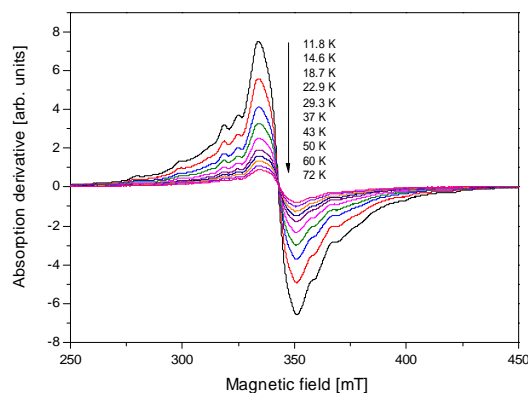


Fig.2. EPR spectra of  $\text{SbVO}_5$  at different temperatures.

The broad line without hfs lines could be attributed to a mobile electron hopping along a  $\text{V}^{4+}\text{-O-V}^{5+}$  bond. The hfs could be substantially suppressed or even disappear due to various interactions of electronic spins with their surroundings. One such interaction occurs via the so-called super-exchange (through oxygen bridge) of an electron between two aliovalent vanadium centres.

As the second EPR spectral component is concerned, it constitutes of two sets of eight lines, partially overlapping, which are due to the interaction of electron spin ( $S=1/2$ ) with  $^{51}\text{V}$  nucleus ( $I=7/2$ ). These spectra could be analyzed by using an axial spin-Hamiltonian of the form:

$$H = \beta \left[ g_{\parallel} B_z S_z + g_{\perp} (B_x S_x + B_y S_y) \right] + A_{\parallel} S_z I_z + A_{\perp} (S_x I_x + S_y I_y) \quad (1)$$

where  $\beta$  is the Bohr magneton,  $g_{\parallel}$ ,  $g_{\perp}$ ,  $A_{\parallel}$ ,  $A_{\perp}$  are the components of the spectroscopic splitting tensor  $g$  and the hyperfine structure tensor  $A$ , respectively.  $B_x$ ,  $B_y$ , and  $B_z$  are components of the magnetic induction vector,  $S_x$ ,  $S_y$ ,  $S_z$  and  $I_x$ ,  $I_y$ ,  $I_z$  are the components of the spin operators of the electron and nucleus, respectively. The

magnetic field positions of the parallel and perpendicular hyperfine peaks, taking into account the second-order perturbation terms, are given by (Agarwal, Seth, Gahlot, Goyal, Arora & Gupta, 2004)

$$\begin{aligned} B_{\parallel}(m) &= B_{\parallel}(0) - mA_{\parallel} - \frac{A_{\perp}^2}{2B_{\parallel}(0)} \left( \frac{63}{4} - m^2 \right) \\ B_{\perp}(m) &= B_{\perp}(0) - mA_{\perp} - \frac{(A_{\parallel}^2 + A_{\perp}^2)}{4B_{\perp}(0)} \left( \frac{63}{4} - m^2 \right) \end{aligned} \quad (2)$$

in which  $m$  is the nuclear spin magnetic quantum number,  $B_{\parallel}(0) = h\nu/g_{\parallel}\beta$ , and  $B_{\perp}(0) = h\nu/g_{\perp}\beta$ .

Measurements for the  $B_{\parallel}$  position were taken to correspond to a maximum in the first derivative curve of the parallel hyperfine structure component for a given  $m$  value, whereas the  $B_{\perp}$  position is enclosed between the first derivative perpendicular peak and its "zero". The  $g$  and  $A$  values calculated from the spectrum are:  $g_{\parallel}=1.9311$ ,  $g_{\perp}=1.9425$  and  $|A_{\parallel}|=181 \cdot 10^{-4} \text{ cm}^{-1}$ ,  $|A_{\perp}|=54 \cdot 10^{-4} \text{ cm}^{-1}$ , and they didn't show any significant temperature dependence. Both  $A_{\parallel}$  and  $A_{\perp}$  were found to be negative. An octahedral site with tetragonal compression would give  $g_{\parallel} < g_{\perp} < g_e$ , where  $g_e=2.0023$  is the  $g$ -factor of free electrons, and  $|A_{\parallel}| > |A_{\perp}|$ . The values of the hyperfine parameters obtained in the present work indicate this relationship and are close to those vanadyl complexes reported in the literature. It is therefore confirmed that  $V^{4+}$  in  $SbVO_5$  exist as  $VO^{2+}$  ions in octahedral coordination with a tetragonal compression and belong to  $C_{4v}$  symmetry, where the vanadyl oxygen forms the apex V-O bond. The ground state of the  $3d^1$  is thus  $d_{xy}$ . Let  $\Delta g_{\perp} = g_{\perp} - g_e$  and  $\Delta g_{\parallel} = g_{\parallel} - g_e$ . The value of  $\Delta g_{\parallel} / \Delta g_{\perp}$  is a good measure of tetragonality of the vanadium site. For  $SbVO_5$  it is equal to 1.19 what indicates on a relative small tetragonal distortion of octahedral coordination.

From the obtained values of the spin-Hamiltonian parameters, the dipolar hyperfine coupling parameter,  $P$ , and the dimensionless Fermi contact interaction term,  $k$ , could be calculated using the relations (Kivelson & Lee, 1964):

$$\begin{aligned} A_{\parallel} &= -P \left[ k + 4/7 - \Delta g_{\parallel} - (3/7) \Delta g_{\perp} \right] \\ A_{\perp} &= -P \left[ k - 2/7 - (11/14) \Delta g_{\perp} \right] \end{aligned} \quad (3)$$

Here  $P$  represents the dipole-dipole interaction of the electronic and nuclear moments given by  $P = 2\gamma\beta\beta_N \cdot \langle r^{-3} \rangle$ , where  $\gamma$  is the gyromagnetic ratio,  $\beta_N$  the nuclear magneton, and  $\langle r^{-3} \rangle$  is calculated for the vanadium  $3d$  orbitals. The value of  $P$  ranges from 100 to  $160 \cdot 10^{-4} \text{ cm}^{-1}$

in various vanadyl complexes. The value of  $k$ , ranging from 0.6 to 0.9, indicates the contribution to the hyperfine coupling due to the isotropic Fermi contact interaction and is very sensitive to small deformations of the metal orbitals. For the vanadyl complex in  $SbVO_5$ ,  $P=140 \cdot 10^{-4} \text{ cm}^{-1}$ ,  $k=0.6244$ . The product  $Pk=87.4 \cdot 10^{-4} \text{ cm}^{-1}$  presents the anomalous contribution of  $s$ -electrons to the  $A_{\parallel}$ ,  $A_{\perp}$  components, the rest being the contribution of  $3d_{xy}$  electrons. The low value of  $k$  in the present system indicates a small contribution to the hyperfine constant by the unpaired  $s$ -electron. The standard value of  $P$  for a free ion is  $160 \cdot 10^{-4} \text{ cm}^{-1}$ . The calculated value in our material is moderately reduced (87%), which indicates a fair amount of covalent bonding in the complex.

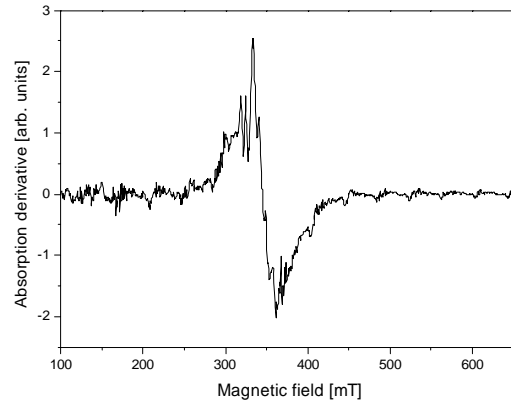


Fig.3. EPR spectrum of  $SbVO_5$  at 3.65 K

In Fig. 3 the EPR spectrum of  $SbVO_5$  recorded at  $T=3.65 \text{ K}$  is shown. This spectrum is typical for a triplet state indicating the presence of two interacting  $VO^{2+}$  with spin  $1/2$  giving a singlet  $S=0$  and a triplet  $S=1$  state. The eight-line pattern is now decomposed into two sets of fifteen lines corresponding to a total nuclear spin of  $I=7$  from the electron exchange between two  $^{51}\text{V}$  nuclei. The sets of lines in the perpendicular region are separated by the zero field-splitting parameter  $D$ , while the parallel sets are separated by  $2D$ . Due the overlap of different components the resulting spectrum is complicated, so only the following dimer parameters could be confidently calculated:  $|A_{\parallel}|=364 \cdot 10^{-4} \text{ cm}^{-1}$ ,  $g_{\parallel}=1.96$ ,  $D=19 \cdot 10^{-4} \text{ cm}^{-1}$ . The appearance of a low-field line ( $B \sim 160 \text{ mT}$  at  $g \approx 4$ ) is yet another manifestation of the presence of dimeric species and is attributed to the forbidden  $\Delta M_s = \pm 2$  transition. The low-field dimer lines are clearly visible in our spectra. The disappearance of dimeric spectra at higher temperature could be explained by rapid broadening caused by shortening of the relaxation time of interactions with the dimer matrix.

The integrated intensity of the EPR spectrum, defined as  $A(\Delta B_{pp})^2$ , where  $A$  is the peak-to-peak amplitude and  $\Delta B_{pp}$  is the peak-to-peak first derivative linewidth, is proportional to magnetic susceptibility of the spin system. As the lineshape and the linewidth of the observed EPR spectrum has not changed in the investigated temperature range, the temperature dependence of signal amplitude reflects the integrated intensity evolution. Figure 4 presents the reciprocal EPR intensity variation in the 4 -100 K temperature range for vanadyl complex in  $\text{SbVO}_5$ . Above 35 K that dependence is described by the Curie-Weiss law,  $I=C/(T-T_{CW})$ , with  $T_{CW}=8$  K. Positive value of  $T_0$  indicates on existence of a weak ferromagnetic interaction between vanadyl complexes.

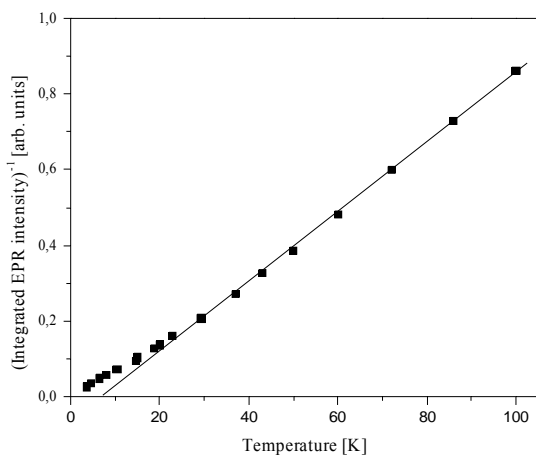


Fig.4. Temperature dependence of the reciprocal integrated EPR intensity for  $\text{SbVO}_5$ .

Magnetic resonance study of the products of thermal decomposition of  $\text{SbVO}_5$  has also been carried out (Typek, Filipek, Maryniak & Guskos, 2005).  $\text{SbVO}_5$  is stable in air up to  $710^\circ\text{C}$  and in argon up to  $\sim 645^\circ\text{C}$ . At higher temperatures it decomposes into a phase with a rutile-type structure. The aim was to gain knowledge on decomposition products of  $\text{SbVO}_5$  and to resolve the problem of the oxidation state of vanadium (3+ or 4+) in these phases. The question of the oxidation states of metal ions in non-stoichiometric rutile-type compounds has been the subject of controversy and is of great importance for the correct interpretation of catalytic mechanisms.

presented. The spectra show similar characteristics: the presence of a very broad line and a relatively narrow resonance line. Taking into account the observed EPR features of the investigated samples, it is proposed that the broad component arises from vanadium(IV) clusters present inside the micrograins forming powder samples, while the narrow component arises from vanadium(IV)

ions located on the surface of these grains. The relative intensity of the broad and narrow components ( $\sim 10^{-3}$ ) reflects the relative number of these centers and also the volume fraction of sample they occupy. This value seems reasonable taking into account the mean grain diameter. As in the  $\text{SbVO}_5$  compound, the bulk of the vanadium is in the 5+ valence state and thus unobservable in EPR spectrum. The heating of  $\text{SbVO}_5$  sample causes the conversion of V(V) to V(IV) and 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. This is indeed what is being observed: oxygen loss is bigger for samples heated in an argon atmosphere and the broad component in the EPR spectrum is more intense.

In Fig.5 room temperature EPR spectra of the decomposition products in air and in argon are presented. The spectra show similar characteristics: the presence of a very broad line and a relatively narrow resonance line. Taking into account the observed EPR features of the investigated samples, it is proposed that the broad component arises from vanadium(IV) clusters present inside the micrograins forming powder samples, while the narrow component arises from vanadium(IV) ions located on the surface of these grains. The relative intensity of the broad and narrow components ( $\sim 10^{-3}$ ) reflects the relative number of these centers and also the volume fraction of sample they occupy. the EPR spectrum is more intense. This value seems reasonable

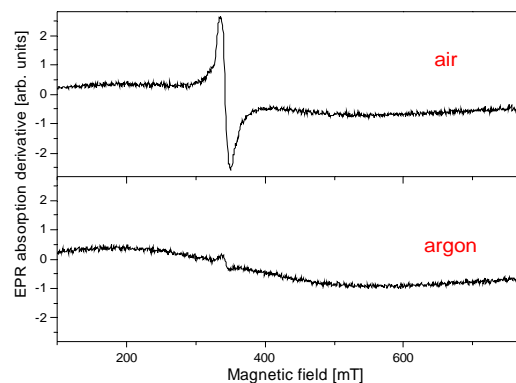


Fig.5. Room temperature EPR spectra of decomposition product of  $\text{SbVO}_5$ : upper panel – decomposition in air, lower panel – decomposition in argon.

taking into account the mean grain diameter. As in the  $\text{SbVO}_5$  compound, the bulk of the vanadium is in the 5+ valence state and thus unobservable in EPR spectrum. The heating of  $\text{SbVO}_5$  sample causes the conversion of V(V) to V(IV) and 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. This is indeed what is being

observed: oxygen loss is bigger for samples heated in an argon atmosphere and the broad component in

### B. $Sb_3V_2Mo_3O_{21}$

EPR spectra of powder samples of  $Sb_3V_2Mo_3O_{21}$  registered at different temperatures in the 4-290 K range are presented in Fig. 6. Single, very broad line is observed. Comparison with  $VOSO_4 \cdot 5H_2O$  intensity standard revealed that only 11.3% of all vanadium ions in  $Sb_3V_2Mo_3O_{21}$  are paramagnetic V(IV) species.

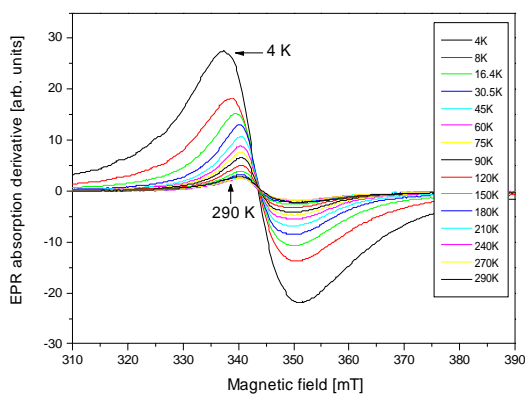


Fig. 6. Selection of EPR spectra of  $Sb_3V_2Mo_3O_{21}$  powder samples registered at different temperatures in the 4-290 K range.

The broad EPR line, arising from strongly interacting paramagnetic vanadium ions, could be decomposed on anisotropic components by using SIMPOW computer program. Using three Lorentzian-shape lines with

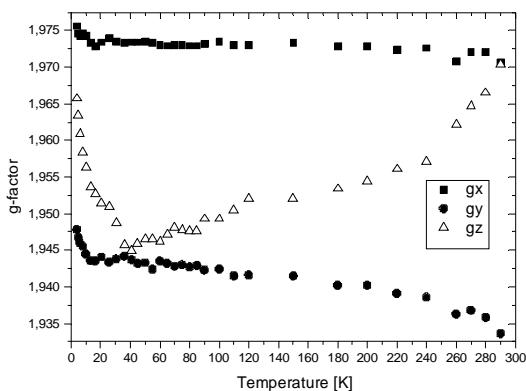


Fig. 7. Temperature dependence of anisotropic  $g$ -factors of  $Sb_3V_2Mo_3O_{21}$  in the 4-290 K range.

different  $g$ -factors and linewidths gave satisfactory fitting to the experimental spectra in the whole investigated temperature range. In this way the temperature dependence of  $g$ -factors and linewidths could be extracted and are presented in Figs. 7 and 8.

The anisotropic  $g$ -factors, and particularly the  $z$  component, vary with temperature in a very interesting manner. The whole investigated temperature range could be divided in two parts: low temperature range,  $T < 40$  K, and high temperature range,  $50 \text{ K} < T < 290$  K. In the low temperature range the linewidths and  $g$ -factors increase significantly with decrease in temperature. In the high temperature range the changes are small, except for the  $z$  component of the  $g$ -factor that varies strongly with temperature.

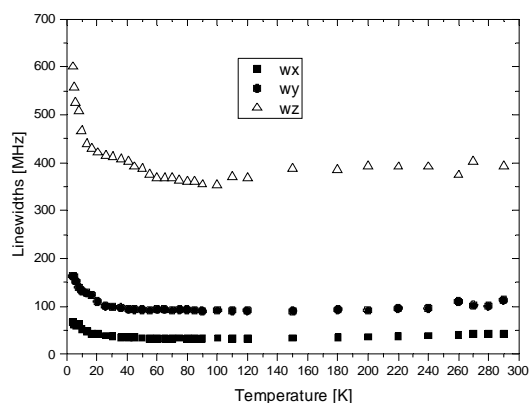


Fig. 8. Temperature dependence of anisotropic linewidths of  $Sb_3V_2Mo_3O_{21}$  in the 4-290 K range.

In Fig. 9 temperature dependence of the EPR integrated intensity, reciprocal of integrated intensity and the product of temperature and integrated intensity is presented. The last quantity is proportional to the square root of an effective magnetic moment. In a broad temperature range ( $30 \text{ K} < T < 150 \text{ K}$ ) the integrated intensity follows the Curie-Weiss law,  $C/(T-T_{CW})$ , with Curie-Weiss constant  $T_{CW} = -9.8$  K. Negative sign of the Curie-Weiss constant indicates on the antiferromagnetic interaction between paramagnetic species. This interaction diminishes the effective magnetic moment what is evident in the decrease of the product of temperature and integrated intensity with temperature decrease (Fig. 9, bottom panel).

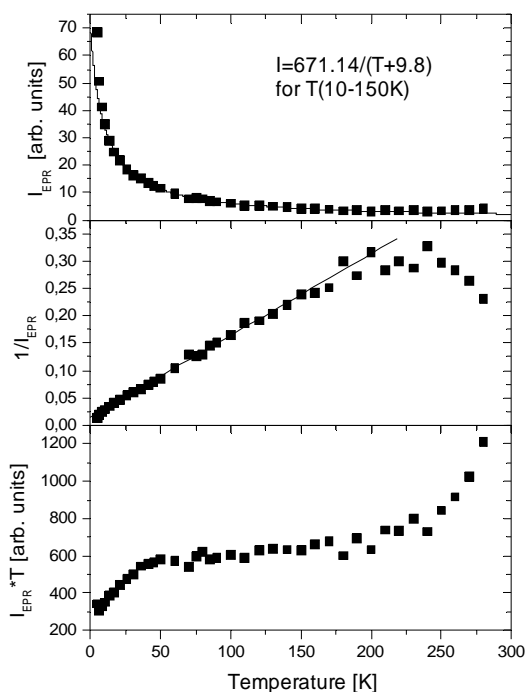


Fig.9. Temperature dependence of the EPR integrated intensity (top panel), reciprocal of integrated intensity (middle panel) and the product of temperature and integrated intensity (bottom panel).

### C. $SbVO_5:MoO_3$ solid solutions

In Fig.10 EPR spectra of six investigated samples of solid solutions of  $MoO_3$  in  $SbVO_5$  are presented. Assuming that the compensation of an excessive positive charge of  $Mo^{6+}$  occurs through formation of cationic vacancies (designated as  $\square$ ) at  $Sb^{5+}$  and  $V^{5+}$  sites, the following formula for solid solution could be written:  $Sb_{1-6x}\square_xV_{1-6x}\square_xMo_{10x}O_5$  (vacancy index  $x=0.0051; 0.0077, 0.0104; 0.0132, 0.0159, 0.0188$ , for samples designated 1-6 in Fig.10).

As expected, the higher the  $MoO_3$  content in solid solution the more intense are the EPR lines. This dependence is not linear, though. This could be seen in Fig.11 (upper panel). Besides, the linewidth decreases with  $MoO_3$  content what indicates an important role of the exchange interaction. That EPR signal intensity

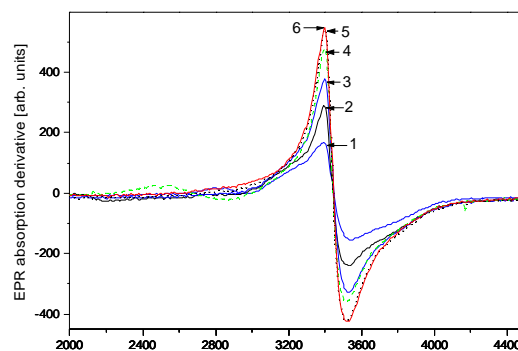


Fig.10. EPR spectra of six investigated samples of  $SbVO_5:MoO_3$  at room temperature

correlates with  $MoO_3$  content means that the charge compensation could not be realized solely by vacancy formation. Another possibility is the valence reduction of  $V^{5+}$  (nonmagnetic)  $\rightarrow V^{4+}$  ion.

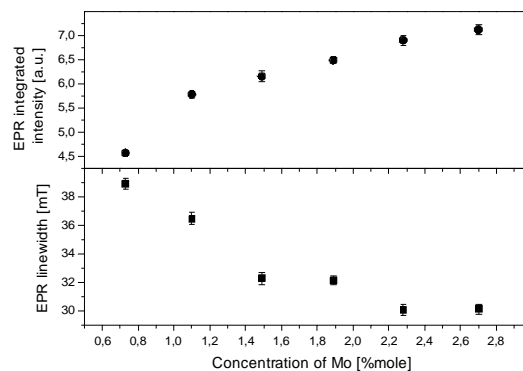


Fig.11. EPR integrated intensity (upper panel) and EPR linewidth (bottom panel) dependence on Mo ion concentration in solid solutions.

Because the observed EPR signal is attributed to the  $V^{4+}$  (or  $VO^{2+}$ ) ions, comparison with  $VOSO_4 \cdot 5H_2O$  intensity standard and analysis of the curve in Fig.11 (upper panel) enabled calculation of the fraction of  $Mo^{6+}$  ions involved in both types of compensation mechanisms. The results are presented in Fig.12.

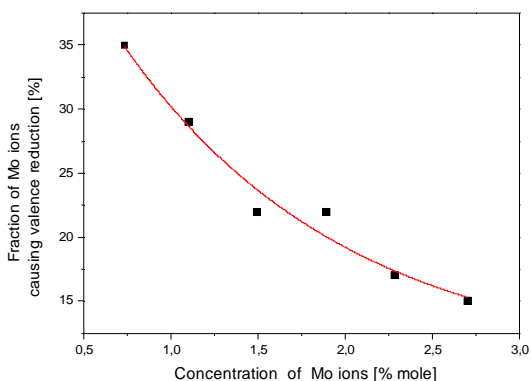


Fig.12. Fraction of Mo ions involved in valence reduction of  $V^{5+}$  ions as a function of total concentration of Mo ions in  $SbVO_5:(MoO_3)_2$  solid solutions.

The obtained results indicate that roughly three quarters of all  $Mo^{6+}$  ions are involved in charge compensation by formation of cation vacancies, the other one quarter takes part in charge reduction of  $V^{5+}$  ions. As the concentration of  $Mo^{6+}$  ions in solid solution increases the last mechanism plays even smaller part in charge compensation.

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