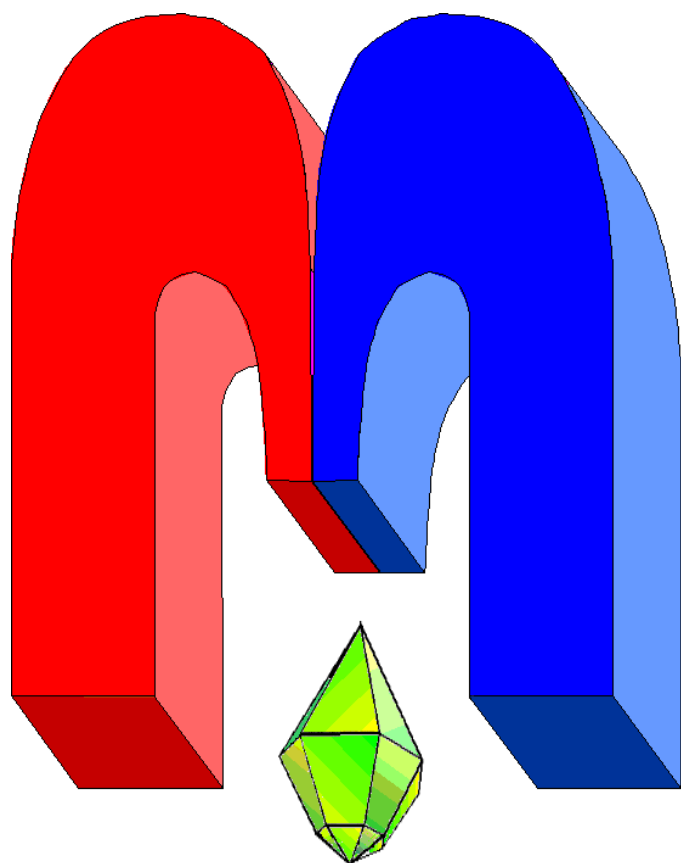


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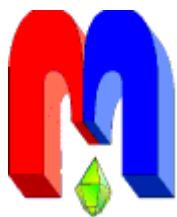
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* In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

EPR of the V^{4+} ion in single crystals of pyrovanadates β - $Mg_2V_2O_7$, α - $Zn_2V_2O_7$: Spin-Hamiltonian parameters

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The angular variation of V^{4+} electron paramagnetic resonance (EPR) line positions were recorded in single crystals of β - $Mg_2V_2O_7$ and α - $Zn_2V_2O_7$ at 120 K and 295 K in three mutually perpendicular planes in the temperature range from 120 to 295 K and at some intermediate temperatures. Least-squares fitting was used by diagonalization of the Spin-Hamiltonian (SH) matrix to determine the SH parameters and the orientations of the principal axes of the \mathbf{g} - and \mathbf{A} -matrices from the angular variations of the EPR line positions. Although the V^{4+} SH parameters were found to be similar in the two crystals, the orientations of the principal axes of the \mathbf{g} - and \mathbf{A} -matrices were not found to be coincident in the two crystals.

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Keywords: V^{4+} ion, Spin-Hamiltonian parameters, \mathbf{g} -matrix, \mathbf{A} -matrix, EPR, pyrovanadates

1. Introduction

Vanadium-mixed oxides (V-Mg-O, V-Zn-O) are important in catalytic processes such as oxidative dehydrogenation of hydrocarbons [1] and selective catalytic reduction of NO by ammonia [2]. The class of vanadia known as vanadates is of great interest now, because these compounds are used in the synthesis of the supported V_2O_7 catalyst [3], insulin-mimetic agents [4] and rechargeable Li batteries [5]. A further point of interest is the thermochromic nature of α - $Zn_2V_2O_7$, which is light yellow in the α phase and changes to red in the β phase [6]. Ioffe *et al.* [7] found that the electrical conductivity of $Mg_2V_2O_7$ and $Zn_2V_2O_7$ pyrovanadates strongly depends on the impurity ions and thermal treatment, which governs the formation of V^{4+} defects. They also obtained qualitative V^{4+} electron paramagnetic resonance (EPR) spectra in Ca, Cd, Mg and Zn pyrovanadates. Crystallochemistry of these compounds was studied experimentally by solid state nuclear magnetic resonance (NMR) [8, 9, 10], and theoretically by using point-monopole approximation and *ab initio* calculations [10, 11]. The Mn^{2+} EPR spectra in single crystals of $Cd_2V_2O_7$ were investigated by Stager [12], whereas the Mn^{2+} EPR spectra in single crystals of $Ca_2V_2O_7$ and $Mg_2V_2O_7$ were investigated by Andronenko *et al.* [13]. Later, the Mn^{2+} EPR spectra in α - $Zn_2V_2O_7$ single crystals were investigated by multifrequency EPR [14]. Recently, the use of nanoparticles of titanium and vanadium oxides as catalysts in Ti-O [15] or V-O [16], has attracted great interest because of its effectiveness in nanostate as compared to that in bulk materials. The doping of catalysts, such as $Mg_2V_2O_7$, with transition metals (Mn, Co, Ni, Fe) also increases its effectiveness [17]. Therefore, investigation of different defects in these compounds, which play a key role in catalysis, is very important to understand the effectiveness of catalytic properties of such oxides.

In this paper we present a precise determination of Spin-Hamiltonian (SH) parameters, specifically the \mathbf{g} - and \mathbf{A} -matrices and the orientation of their principal axes of V^{4+} ions in β - $Mg_2V_2O_7$ and α - $Zn_2V_2O_7$ single crystals, and a determination of the position of V^{4+} ions in the crystal structure.

2. Sample preparation and crystal structure

Synthesis

The phase diagrams of ZnO- V_2O_5 and MgO- V_2O_5 systems were investigated to determine the conditions of crystallization of low and high-temperature phases of $Zn_2V_2O_7$ and $Mg_2V_2O_7$ [18, 19]. Single crystals of $Zn_2V_2O_7$ and $Mg_2V_2O_7$ were grown by the spontaneous-crystallization method during slow cooling of the melt with stoichiometric composition using the chemicals V_2O_5 (extreme pure), ZnO (chemically

pure) and $MgCO_3$ (chemically pure). Crystals of $Zn_2V_2O_7$ grew as large rectangular slabs with well-defined (110) cleavage planes. All crystals were twinned, as determined by X-ray diffraction. The growth habits of $Zn_2V_2O_7$ and $Mg_2V_2O_7$ single crystals are shown in Fig. 1 with respect to the orientations of respective laboratory axes XYZ . Note, that the authors of [10] investigated NMR spectra of both α and β - $Mg_2V_2O_7$ crystals at room temperature, where β - $Mg_2V_2O_7$ was obtained from α - $Mg_2V_2O_7$ simply with annealing at $850^\circ C$ during 48 hours, followed by rapid cooling to room temperature. Therefore, the phase transition becomes irreversible and the high-temperature phase is stable at room temperature.

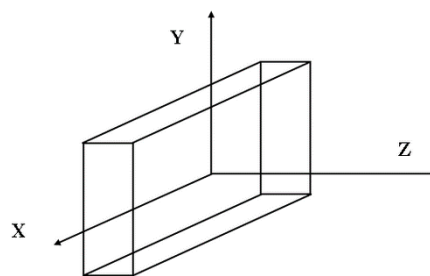


Figure 1. The crystal growth habits of $Mg_2V_2O_7$ and $Zn_2V_2O_7$ crystals in relation to the laboratory axes XYZ .

Crystal structure of $Zn_2V_2O_7$

The $Zn_2V_2O_7$ crystal undergoes a fast reversible structural phase transformation at $615^\circ C$ from the high-temperature thortveitite β -phase (HT phase) with the space group $C2/m$ to the low-temperature α -phase (LT phase) of $Zn_2V_2O_7$, possessing monoclinic symmetry characterized by the space group $C2/c$ with the unit-cell parameters: $a = 7.429 \text{ \AA}$, $b = 8.340 \text{ \AA}$, $c = 10.098 \text{ \AA}$ and $\beta = 114.4^\circ$ and $Z = 4$ [20]. The main difference between the high (HT) and low (LT) temperature phase structures is that in the former the coordination of Zn ions is six-fold, while in the latter the cations reduce their coordination to five oxygen atoms. In the LT-phase, the ZnO_5 group is a distorted trigonal bipyramid with the longer Zn-O bonds oriented in the axial direction. Vanadium and oxygen ions form V_2O_7 pyrogroups in the structure of α - $Zn_2V_2O_7$. The low-temperature structure contains layers of oxygen atoms stacked perpendicular to the [001] axis, and Zn ions and V-O-V groups lie in octahedrally coordinated sites in alternate layers of oxygen atoms.

Crystal structure of $Mg_2V_2O_7$

The high-temperature β -phase of $Mg_2V_2O_7$ was synthesized at higher temperatures, $T > 800^\circ C$, above the phase transition between α - and β -phases, at $T = 760^\circ C$ [21]. This phase is stable at room temperature and possesses triclinic space symmetry $P\bar{1}$, with the unit-cell parameters being: $a = 13.767 \text{ \AA}$, $b = 5.414 \text{ \AA}$, $c = 4.912 \text{ \AA}$, $\alpha = 81.42^\circ$, $\beta = 106.82^\circ$, $\gamma = 130.33^\circ$, $Z = 2$ [22]. Only the high-temperature β -phase was investigated here, which remains stable at room temperature. although it is below the phase-transition temperature. The structure of β - $Mg_2V_2O_7$ consists of chains of V_2O_7 groups formed from two VO_4 tetrahedra, which share one common oxygen ion. The adjacent V_2O_7 chains form sheets lying in the (001) plane. They are separated by Mg cations which share oxygen atoms with these sheets.

3. The local structure of V^{5+} ions in $V_2O_7^{4-}$ pyrogroups

The V^{4+} and O^{2-} ions compose $V_2O_7^{4-}$ pyrogroups, which consist of two VO_4 tetrahedra, connected through common O^{2-} ion. This pyrogroup is shown for β - $Mg_2V_2O_7$ in Fig. 2. The point symmetry of the ion in $Mg_2V_2O_7$ is C_i and there are two structurally inequivalent sites for V^{5+} ions in its lattice. In this pyrogroup one V^{5+} ion is 5-fold coordinated and the second V^{5+} ion is 4-fold tetrahedrally coordinated. The corresponding quadrupole coupling parameters (C_Q and η_Q) are different for these two vanadium nuclei, $C_Q = 10.1 \text{ MHz}$ for the 5-fold coordinated vanadium ions, much larger, than that for the other 4-fold coordinated vanadium ion ($C_Q = 4.8 \text{ MHz}$) [9, 10]. There is only one structurally inequivalent site for V^{5+} ions in the $Zn_2V_2O_7$ structure with the point symmetry C_i . The vanadium ion is 4-fold coordinated and the V-O bond lengths as well as the value for $C_Q = 3.9 \text{ MHz}$ [10] are similar to those in $Mg_2V_2O_7$ for the 4-fold coordinated ion. Therefore, similar the V^{4+}

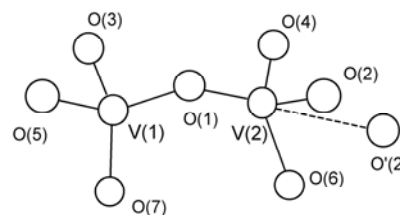


Figure 2. The pyrogroup V_2O_7 in β - $Mg_2V_2O_7$ and α - $Zn_2V_2O_7$ crystals (without O^{2-}).

hyperfine (HF) EPR spectra are expected for the V^{4+} ion in these sites in both $Mg_2V_2O_7$ and $Zn_2V_2O_7$ single crystals, and, thus, similar values for V^{4+} hyperfine parameters and the orientations of their principal axes are also expected. The second structurally inequivalent V^{5+} ion, which is situated in distorted tetrahedral configuration associated with the fifth oxygen ion was not observed by EPR in $Mg_2V_2O_7$. Ioffe *et al.* [7] observed another V^{4+} EPR spectrum in $Mg_2V_2O_7$ after annealing it in reduced atmosphere (CO or NH_3 gas at $450^\circ C$). They deduced that each hyperfine line of the V^{4+} EPR spectrum split into 8 components by the superhyperfine (SHF) interaction ($A_{SHF} = 6$ G) with the nearby vanadium nuclei. However, such EPR spectrum was not observed in the presently investigated $Mg_2V_2O_7$ single crystal. The formation of V^{4+} ions ($3d^1$ state) in V-O polyhedra, in which the vanadium ion is in 5-valent state, can be due to the presence of uncontrolled nonmagnetic impurities, or proton (H^+) as an impurity [7]. The EPR spectra for the V^{4+} ion have been observed in many vanadium compounds (CaV_2O_6, V_2O_5) [23, 24]. On the other hand, the V^{4+} EPR spectra were not observed in orthovanadates ($YVO_4, PrVO_4$) [25], implying that the V^{5+} state is stable in 4-fold configuration of VO_4 polyhedra.

4. V^{4+} EPR spectra: determination of SH parameters

Experiment

A Bruker ER-200D SRC EPR X-band spectrometer equipped with nitrogen-flow Bruker variable temperature assembly was used to investigate the EPR spectra in single crystals of β - $Mg_2V_2O_7$ and α - $Zn_2V_2O_7$. Usual setting of EPR spectrometer: modulation field is 1-5 G / 100 kHz and microwave power is 20 Db (max output power is 200 mW). The EPR spectra of the V^{4+} ions were recorded at X-band (9.6 GHz) in the temperature range 120-300 K. Only one magnetically inequivalent V^{4+} ion was observed in the two crystals in the temperature range accessible in the present experiment. Detailed angular variations of V^{4+} X-band EPR line positions were recorded at 120 K and 290 K in three mutually perpendicular planes in the two single crystals. They are shown in Figs. 3a,b,c and 3d,e,f respectively. The angular variations of V^{4+} X-band EPR spectra recorded at 290 K in three mutually perpendicular planes in β - $Mg_2V_2O_7$ single crystal are similar to those shown in Figs. 3 for α - $Zn_2V_2O_7$ single crystal, and not shown here. In each plane, the magnetic field orientation was varied at 5° intervals. The orientation of the principal axes corresponding to the largest principal g -value, i.e. the direction of the Zeeman field for which the positions of the lines are at their minimum, in this plane was chosen to be the magnetic Z' -axis, which was found to be approximately perpendicular to largest flat surface of the crystal. The Z -axis and Z' -axis are not coincident. For EPR measurements in the laboratory ZY and XY planes the specimen was oriented in such a way that it could be rotated about the X and Z -axes, keeping the external static magnetic field fixed.

Spin-Hamiltonian parameters

The spin-Hamiltonian of the V^{4+} ion, describing the interaction of its magnetic moment with the external magnetic field \mathbf{B} , and the hyperfine (HF) interaction with its own ^{51}V nucleus, is written in following form [26]:

$$H = \mu_B \mathbf{B} \mathbf{g} \mathbf{S} + \mathbf{S} \mathbf{A} \mathbf{I}, \quad (1)$$

where μ_B is the Bohr magneton, $S = 1/2$ is electronic spin of the V^{4+} ion, and \mathbf{g} is the \mathbf{g} -matrix, [26]. The ^{51}V nucleus (99.76% natural abundance) has the nuclear spin $I = 7/2$ ($g_n = 1.468$); thus, each line splits into eight HF lines at X-band. In Eq. (1) \mathbf{A} is HF interaction matrix; the principal axes of the \mathbf{g} and \mathbf{A} matrices are, in general, not coincident with each other for low (monoclinic and triclinic) symmetries. A rigorous least-squares fitting of EPR line positions in three mutually perpendicular planes to the SH parameters enabled determination of the orientations of the principal axes of the \mathbf{g} and \mathbf{A} matrices [27, 28]. Two fitting programs were used here in the evaluation of the SH parameters, one for fitting the principal values and their orientations of the \mathbf{g} -matrix and the second one for fitting the principal values of the \mathbf{A} matrix. The results are listed in Tables 1-6.

The orientations of the principal axes of the \mathbf{g} -matrix are denoted as $Z'X'Y'$, whereas the principal axes of the \mathbf{A} -matrix are denoted as $Z''X''Y''$. The principal values of \mathbf{g} are dimensionless, while those of \mathbf{A} are expressed in GHz. The indicated errors are estimated by the use of a statistical method as outlined

by Misra and Subramanian [29]. The direction cosines of the principal axes of the g -matrix (X' , Y' , Z') are given with respect to the laboratory, XYZ -axes defined in section 2, whereas those of the A -matrix ($X''Y''Z''$) are expressed relative to ($X'Y'Z'$).

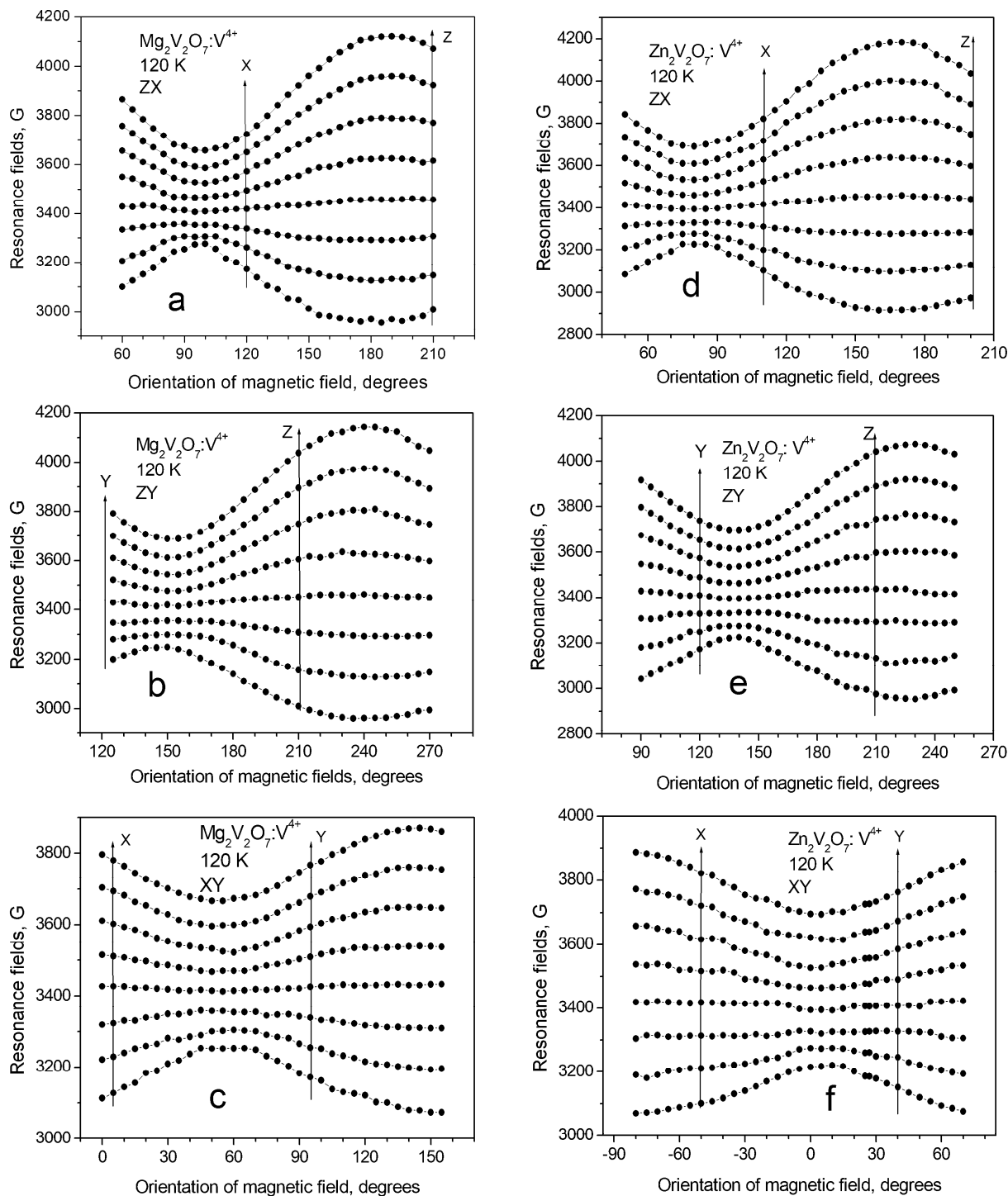


Figure 3. Angular variations of the V^{4+} EPR spectra at 120 K in single crystals of $Mg_2V_2O_7$ and $Zn_2V_2O_7$, respectively, in three mutually perpendicular planes in the laboratory coordinate system; panels (a) and (d) correspond to ZX; (b) and (e) correspond to ZY; (c) and (f) correspond to XY.

Temperature dependence and unresolved SHF splitting

The EPR spectra in the temperature range from 120 to 295 K for the specific orientations of the magnetic fields in β - $Mg_2V_2O_7$ and α - $Zn_2V_2O_7$ are shown in Figs. 4a and 4b, respectively. The EPR spectra were recorded for $Mg_2V_2O_7$ for the orientations of the external magnetic field in the ZY plane, whereas those

for $Zn_2V_2O_7$ for the orientations of the external magnetic field in the ZX plane. There was observed no significant temperature dependence of the EPR linewidth for V^{4+} ions in the temperature range 120-290 K. The average V^{4+} EPR linewidth is rather large, about 30-35 G. It is due to the superhyperfine (SHF) interaction of spin of the V^{4+} ion with nearest V nucleus ($I = 7/2$), which splits each HF line into eight unresolved SHF lines. If the individual EPR linewidth is larger than 5 G, then unresolved SHF structure will appear. The SHF interaction constant can be estimated to be 5-6 G, which is reasonable, similar to that observed by Ioffe *et al.* [7] in pyrovanadates for the “second” EPR V^{4+} center ($A_{SHF} = 6$ G).

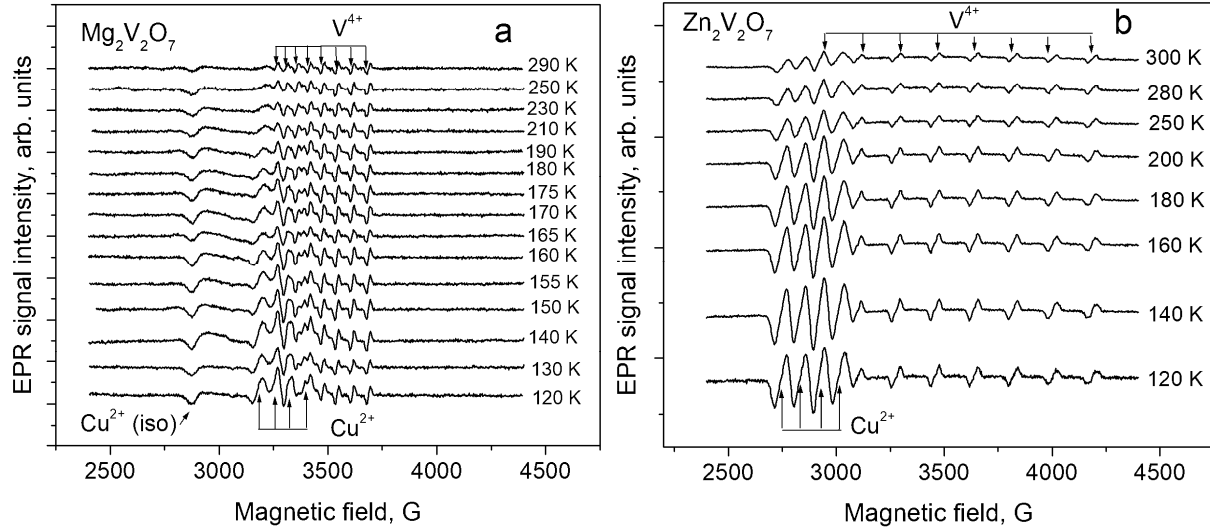


Figure 4. The EPR spectra in $Mg_2V_2O_7$ and $Zn_2V_2O_7$ single crystals at various temperatures for the particular orientation of the external magnetic field. Fig. 4a: $\beta = 150^\circ$, ZY plane (as shown in Fig. 3b), minimum HF splitting and Fig. 4b: $\alpha = 170^\circ$, ZX plane (as shown in Fig. 3d), maximum HF splitting, respectively. The EPR lines for Cu^{2+} , also present as impurity, are seen at lower magnetic fields.

Table 1. The principal values of the g -matrices of the V^{4+} ions in single crystals of β - $Mg_2V_2O_7$ and α - $Zn_2V_2O_7$ at 120 K and 290 K. The numbers of V^{4+} EPR lines fitted to EPR line positions at 120 and 290 K under consideration in β - $Mg_2V_2O_7$ are 808 and 744, and those in α - $Zn_2V_2O_7$ are 768 and 768. $SMD (GHz^2) \equiv \sum_i (\Delta E_i/h - \nu_i)^2$, where (ΔE_i) is the calculated energy difference in GHz between the levels participating in resonance for the i^{th} line position; ν_i is the corresponding klystron frequency in GHz, h is Planck’s constant; $RMSL(GHz) = (SMD/n)^{1/2}$ is average mean-square deviation of energy level difference from klystron frequency.

	Temperature (K)	g_z	g_x	g_y	n	RMSL (GHz)
$Mg_2V_2O_7$	295	1.930 ± 0.001	1.977 ± 0.001	1.996 ± 0.001	744	0.006
	120	1.932 ± 0.001	1.969 ± 0.001	2.002 ± 0.001	808	0.011
$Zn_2V_2O_7$	295	1.928 ± 0.001	1.969 ± 0.001	2.013 ± 0.001	768	0.016
	120	1.932 ± 0.001	1.976 ± 0.001	2.011 ± 0.001	768	0.014

Table 2. The principal values of the A -matrices of the V^{4+} ions in single crystals of β - $Mg_2V_2O_7$ and α - $Zn_2V_2O_7$ at 120 K and 295 K.

	Temperature (K)	A_z (GHz)	A_x (GHz)	A_y (GHz)	n	RMSL (GHz)
$Mg_2V_2O_7$	295	0.480 ± 0.005	0.185 ± 0.005	0.147 ± 0.005	744	0.058
	120	0.490 ± 0.005	0.170 ± 0.005	0.156 ± 0.005	808	0.055
$Zn_2V_2O_7$	295	0.504 ± 0.005	0.189 ± 0.005	0.170 ± 0.005	768	0.083
	120	0.500 ± 0.005	0.194 ± 0.005	0.179 ± 0.005	768	0.060

Table 3. The principal values and direction cosines of the principal axes of the \mathbf{g} -matrices for the V^{4+} ions in single crystals of β - $Mg_2V_2O_7$ at 120 K and 295 K.

Temp. (K)	g_z, g_x, g_y	Direction cosines		
		Z/Z'	X/X'	Y/Y'
295	$g_z = 1.930$	0.924	0.210	0.318
	$g_x = 1.977$	-0.105	-0.660	0.744
	$g_y = 1.996$	-0.366	-0.721	0.588
120	$g_z = 1.932$	0.927	-0.083	-0.365
	$g_x = 1.969$	0.215	-0.680	0.701
	$g_y = 2.002$	0.306	0.729	0.612

Table 4. The principal values and direction cosines of the principal axes of the \mathbf{A} -matrices for the V^{4+} ion in a single crystal of β - $Mg_2V_2O_7$ at 120 K and 295 K.

Temp. (K)	A_z, A_x, A_y	Direction cosines		
		Z/Z'	X/X'	Y/Y'
295	$A_z = 0.480$	0.863	0.433	-0.260
	$A_x = 0.185$	-0.424	0.901	0.094
	$A_y = 0.147$	0.275	0.029	0.961
120	$A_z = 0.490$	0.891	-0.359	0.278
	$A_x = 0.170$	0.241	0.893	0.381
	$A_y = 0.156$	-0.385	-0.272	0.882

Table 5. The principal values and direction cosines of the principal axes of the \mathbf{g} -matrices for the V^{4+} ion in a single crystal of α - $Zn_2V_2O_7$ at 120 K and 295 K.

Temp. (K)	g_z, g_x, g_y	Direction cosines		
		Z'/Z''	X'/X''	Y'/Y''
295	$g_z = 1.928$	0.780	0.373	-0.502
	$g_x = 1.969$	0.623	-0.537	0.569
	$g_y = 2.013$	0.057	0.757	0.651
120	$g_z = 1.932$	0.846	0.294	-0.444
	$g_x = 1.976$	0.528	-0.570	0.629
	$g_y = 2.011$	0.068	0.767	0.638

Table 6. The principal values and direction cosines of the principal axes of the \mathbf{A} -matrices for the V^{4+} ion in a single crystal of α - $Zn_2V_2O_7$ at 120 K and 295 K.

Temp. (K)	A_z, A_x, A_y	Direction cosines		
		Z'/Z'	X'/X''	Y'/Y''
295	$A_z = 0.504$	0.944	-0.057	0.324
	$A_x = 0.189$	-0.269	-0.434	0.860
	$A_y = 0.170$	-0.189	-0.899	0.394
120	$A_z = 0.500$	0.966	-0.031	0.258
	$A_x = 0.194$	-0.086	0.899	0.430
	$A_y = 0.180$	-0.246	0.437	0.865

5. Coordination of the V^{4+} ion ($3d^1$) in VO_4 polyhedra

The point symmetry of the vanadium ion is C_i in $Mg_2V_2O_7$ for the two magnetically inequivalent sites for V^{5+} ions. The V^{5+} ion is situated in the first VO_4 tetrahedron, V(1) is 4-fold tetrahedrally coordinated, with the V(1) – O(n) bonding lengths varying from 1.682 to 1.784 Å. The V^{5+} ion is situated in the second VO_4 tetrahedron, V(2), with the bonding lengths from 1.629 to 1.817 Å [22]. It is distorted with the additional bonding to the fifth oxygen ion (V(2) – O(5), with the bonding length being 2.44 Å [22]). In α - $Zn_2V_2O_7$, the V^{5+} ion possesses C_i point symmetry. There is only one magnetically inequivalent site for the V^{4+} ion, which occupies a V^{5+} site. This V^{4+} ion, situated at a regular V^{5+} site, is 4-fold tetrahedrally coordinated with the bonding lengths varying from 1.658-1.775 Å [20]. The $3d^1$ configuration of the V^{4+} ion is split in cubic crystal field into a Γ_3 doublet and a Γ_5 triplet [26]. In tetrahedral coordination, the Γ_3 doublet lies lower, representing the ground state [26]. The spin-orbit coupling constant λ is positive for tetrahedral coordination. Further, the Γ_3 doublet is split into a Γ_1' singlet (wavefunction $|3z^2 - r^2\rangle$) and Γ_3' singlet (wavefunction $|x^2 - y^2\rangle$) [26]. Unfortunately, the V^{4+} ion possesses a very low symmetry in β - $Mg_2V_2O_7$ and α - $Zn_2V_2O_7$ crystals, thus, it is not possible to

determine its actual ground state wavefunction from the available experimental data. The principal values of the **g**- and **A**-matrices, obtained here for $\text{Mg}_2\text{V}_2\text{O}_7$ and $\text{Zn}_2\text{V}_2\text{O}_7$ are close to those obtained by Ioffe *et al.* [23] for the V^{4+} ion in $\text{Ca}_2\text{V}_2\text{O}_7$ single crystal, which is isostructural to the triclinic $\text{Mg}_2\text{V}_2\text{O}_7$ (with the parameters $g_z = 1.948$; $g_x = 1.966$; $g_y = 1.975$; and $A_z = 0.475$ GHz; $A_x = 0.150$ GHz; $A_y = 0.138$ GHz), from which they determined the ground state function of the V^{4+} ion to be $|x^2 - y^2\rangle$. They did not determine the orientations of the principal axes of **g**- and **A**-matrices.

The principal values of the **g**- and **A**-matrices are very similar to each other for the V^{4+} ions in $\text{Mg}_2\text{V}_2\text{O}_7$ and $\text{Zn}_2\text{V}_2\text{O}_7$ single crystals. This is because the V(1) ion in $\text{Mg}_2\text{V}_2\text{O}_7$ is 4-fold coordinated and the average bonding length V(1)–O(n) is 1.730 Å, very close to the average bonding length V–O(n) in $\text{Zn}_2\text{V}_2\text{O}_7$, which is 1.716 Å. The values of **g**- and **A**-matrices depend strongly on overlap of the wave functions of the V^{4+} ions and neighboring oxygen ligands. Therefore, one can deduce that the V^{4+} ion occupies the V(1) crystallographic position in $\text{Mg}_2\text{V}_2\text{O}_7$ single crystals. This conclusion was supported by NMR of ^{51}V nucleus in $\beta\text{-Mg}_2\text{V}_2\text{O}_7$ and $\alpha\text{-Zn}_2\text{V}_2\text{O}_7$ [9, 10]. The values for quadrupole coupling parameters are: $C_Q = 4.8$ MHz for V(1) and $C_Q = 10.1$ for V(2) in $\beta\text{-Mg}_2\text{V}_2\text{O}_7$ and $C_Q = 3.68$ MHz for $\alpha\text{-Zn}_2\text{V}_2\text{O}_7$ [9, 10]. Both the V(1) ion in $\beta\text{-Mg}_2\text{V}_2\text{O}_7$ and the V ion in $\alpha\text{-Zn}_2\text{V}_2\text{O}_7$ are 4-fold coordinated and possess similar values of C_Q . This result was proved also by theoretical calculations of C_Q [11]. Therefore, the environments of V(1) in $\beta\text{-Mg}_2\text{V}_2\text{O}_7$ and V ions in $\alpha\text{-Zn}_2\text{V}_2\text{O}_7$ are similar and the V^{4+} ions, which occupy these sites, expect to have similar SH parameters. The orientations of the principal axes of the **g**-matrices Z' , X' , Y' of the V^{4+} ions relative to the crystal faces are also similar in the two crystals, with the Z' -axis being perpendicular to the (110) cleavage plane (XY plane, see Fig. 1) for $\alpha\text{-Zn}_2\text{V}_2\text{O}_7$, which implies that the cleavage plane of $\text{Mg}_2\text{V}_2\text{O}_7$ is also the (110) plane.

The V^{4+} EPR spectra in several vanadium compounds have been observed over a very large temperature range up to room temperature. For its temperature stability the $\text{O}_3 - \text{V}^{4+} - \text{O} - \text{V}^{5+} - \text{O}_3$ pyrogroupp should be charge-compensated with the positive charge being in the vicinity. Ioffe *et al.* [7] indeed showed that the charge compensation is due to proton (H^+) being in an interstitial position to render the V^{4+} ion stable.

6. Conclusions

The main conclusions of the V^{4+} EPR investigations in $\beta\text{-Mg}_2\text{V}_2\text{O}_7$ and $\alpha\text{-Zn}_2\text{V}_2\text{O}_7$ single crystals are as follows:

- (i) The principal values of the **g** and **A** matrices of the V^{4+} ion and their orientations relative to the crystal faces system have been determined in these crystals.
- (ii) The SH parameters of the V^{4+} ion in $\beta\text{-Mg}_2\text{V}_2\text{O}_7$ and $\alpha\text{-Zn}_2\text{V}_2\text{O}_7$ single crystals are found to be similar because the V^{4+} ions occupy similar tetrahedrally coordinated crystallographic sites in them.
- (iii) The principal axes of the **g**-matrix are not coincident with those of the **A**-matrix because of the low point symmetry C_i .

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