Chem Rep, 2020, 2(1): 124-131
DOI: 10.25082/CR.2020.01.002

RESEARCH ARTICLE

Effect of gamma irradiation on $NaVO_3$ in polycrystalline solid state

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Abstract: An EPR study of the paramagnetic centers formed by γ irradiation of polycrystalline $NaVO_3$, at 77 K and room temperature was performed. According to their EPR parameters and thermal behaviour, the centers were attributed to: $V\dot{O}_3$, $V\dot{O}_3^{2-}$, VO, VO^+ and $\dot{O}_2^-$ radicals. The spin-spin relaxation time was calculated from the derivative peak-to-peak line widths assuming Lorentzian lines. A mechanism of the paramagnetic species formation was proposed.

Keywords: spin-lattice and spin-spin relaxation time, fine structure, hyperfine splitting

1 Introduction

Electron paramagnetic resonance (EPR) spectroscopy has been intensely used to investigate vanadium compounds in both naturally containing vanadium species and spin-labeled or metal substituted systems. The compounds containing vanadium present relevant antidiabetic properties. One of the first uses of the vanadyl ion as a spin probe was with the hormone insulin. Vanadium (IV), almost always found as the highly stable oxocation VO^{2+}, is a Kramers doublet, S=1/2 system, that is very well suited to EPR studies. Vanadium (IV) is rarely found without an oxo ligand. The near-square pyramidal structure of most VO^{2+} complexes yields an orbitally nondegenerate d_{xy} ground state with no low-lying excited states. This leads to slow relaxation behavior in EPR and allows for observation of vanadyl signals at ambient temperatures. Such spectra provide additional structural and/or dynamic information[1].

Vanadium is a transition metal widely distributed in environment. It has been found that vanadate-containing compounds have potent toxic and carcinogenic effects, such as DNA damage and cell transformation[2, 3] .

Radiation (gamma radiation, X-rays, electron beam) can induce numerous changes in the physical properties of the studied compounds, one of the most obvious effects being visible coloration, which is caused by the color centers (defects). Also, irradiation influences the formation and the alteration of the structure and morphology of the crystals[4].

This paper presents comparative results of the $NaVO_3$ characterization, provided by different manufacturing companies (Merck and Riedel-de Haën).The spectral and thermal behaviour after irradiation using the EPR method was investigated.

The goal of this work was to link a structural study of $NaVO_3$ to a characterization of the electronic configuration of V as a function of absorbed dose.

Moreover, this work tries to give the answer as to how the results using the EPR method connected with the structure of the investigated material should be interpreted. It also helps to better understand physical properties of this compound.

The excess of population of the ground state (m_s=-1/2) over that in the upper state (m_s=+1/2), for a single spin system, is extremely small. At a temperature of 300 K the excess population in the ground state is only about 0.07%, yet the whole phenomenon of EPR absorption depends on this difference. The "a priori" probability of transitions upwards equals that for transitions downwards, therefore if the unpaired spin were isolated from their surroundings, the two levels would rapidly become equally populated and the absorption ceases[5].

There must therefore be other mechanism by which energy absorbed and stored in the upper state can be dissipated in such a manner as to permit return to the ground state. Such a mechanism is called relaxation process[6].

The spin-lattice relaxation implies interaction between the spin system and surrounding molecules[7]. The spin-lattice relaxation is characterized by a relaxation time

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Received: February 21, 2020 **Accepted:** March 19, 2020 **Published:** March 23, 2020

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Citation: Neacsu A, Stanciu AE, Contineanu M, *et al.* Effect of gamma irradiation on $NaVO_3$ in polycrystalline solid state. *Chem Rep*, 2020, **2**(1): 124-131.

T_1 which is the time for the spin system to lose 1/e^{th} of its excess energy[8]. In the real system the line width is modified by of other factors.

The most important of these are spin-spin or dipolar interactions, which cause broadening, because each dipole, electronic or nuclear, produces a magnetic field at each its neighbours. Thus, the total magnetic field experienced by a particular spin will include contributions from all its neighbours and will differ from the applied field.

Thus, transitions will occur over a range of frequencies corresponding to the variation of local field from spin to spin. Spin-spin relaxation processes may be characterized by a relaxation time T_2' corresponding to a line width of 1/T_2'[9].

The special case of interaction with other spins within the same atom or molecule may result from the appearance of the fine structure. The fine structure arises in species with more than one unpaired electron.

2 Experimental

The polycrystalline samples of $NaVO_3$ (Merck and Riedel-de Haën) have been irradiated with gamma rays at 77 K and room temperature by using a ^{137}Cs source, having 2.3×10^{13} Bq activity and a dose rate of 1.05×10^{2} Gy/h. The EPR spectra were recorded with an EPR spectrometer ART 5 that operates in the band X, having a frequency modulation of 100 kHz. For calculation of the g factor the ion Mn^{2+} in CaO matrix, as a standard, was used.

3 Results and discussion

The EPR spectrum of a radical with a Lorentzian line has the characteristic form shown in Figure 1(a). The two peaks of the derivative curve (Figure 1(b)) correspond to point of maximum slope in absorption, and separation between them is ΔHpp, for Lorentzian line.

The total line width 1/T_2 parameter consists of two contributions. One, equal to 1/T_1 comes from spin-lattice relaxation, while another part called 1/T_2' comes from spin-spin relaxation. T_2 is taken as the total line width parameter. It is to point out that an order of magnitude relaxation between T_2', T_1 and T_2[10] is Equation (1):

$$\frac{1}{T_2}=\frac{1}{T_2'}+\frac{1}{T_1} \tag{1}$$

In solid, major source of line broadening is the dipol-dipol interactions between neighbouring electron spin. Spin-lattice relaxation time T_1, for free radicals in solid matrices is extremely long because there is little molecular motion compared with those for paramagnetic ions[11].

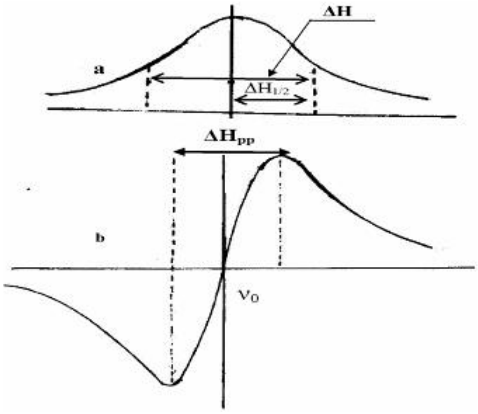


Figure 1. Lorentzian line shape: (a) absorption spectrum; (b) first derivative spectrum

For many systems, especially for the stable free radicals, $T_1 \gg T_2$' and $T_2 \approx T_2$'.

The shape of the line is characterized by a single parameter $T_2{}^{-1}$, which is the half breadth between points of maximum slope[12].

The absorption line centered at the resonance frequency $g\upsilon_0 = \beta H_0/h$ has a finite width and can be represented by a function $f(\upsilon\text{-}\upsilon_0)$ with a maximum at $\upsilon=\upsilon_0$ (Figure 1) normalized so that $\int_0^\infty f(\upsilon-\upsilon_0)=1$. Such a function may be expressed in terms of a characteristic line width, the half-width at half maximum absorption $\Delta H_{1/2}$, expressed in Figure 1(a).

The condition for resonance in an EPR experiment is defined by Equation (2):

$$h\upsilon_{1/2} = g\beta\Delta H_{1/2} \tag{2}$$

where:

$$\Delta\upsilon_{1/2}=\frac{1}{2\pi T_2} \qquad \Delta H_{1/2}=\frac{\sqrt{3}}{2}\Delta H_{pp} \tag{3}$$

Entering Equation (3) in Equation (2) results:

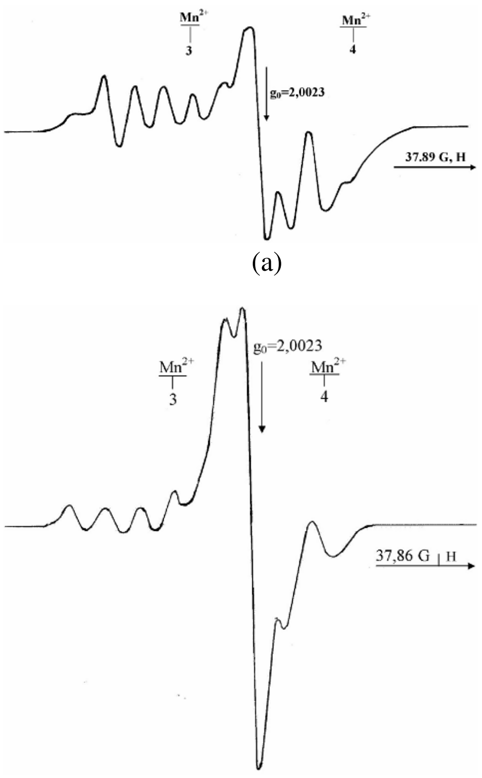
$$T_2=\frac{2\hbar}{\sqrt{3}g\beta\Delta H_{pp}} \tag{4}$$

where: $e\hbar = 1.0544\times10^{-27}$rg/sec,Planck's constant,β = 9.27×10^{-21}erg/Gauss, Bohr magneton, g-spectroscopic splitting factor.

Entering these constants in Equation (4) results the Equation (5):

$$T_2=\frac{1.31\times10^{-7}}{g\Delta H_{pp}} \tag{5}$$

Analyzing the experimental factors that contribute to the broadening of VO^{2+} radical-anion spectral lines, Willson and Kivelson[13] have developed a theory that leads to the Equation (4).



(a)

(b)

Figure 2. EPR spectra of $NaVO_3$ irradiated at 77 K with a dose of 5.3×10^3 Gy: (a) Merck; (b) Riedel-de Haën

In Figure 2(a) and 2(b) there are shown the EPR spectra of the $NaVO_3$ Merck and Riedel-de Haën samples, gamma irradiated, in polycrystalline state, at 77 K and recorded at the same temperature

From Figure 2 it can be seen that the EPR spectra show four well resolved components from the odd electron interaction with ^{51}V nucleus (7/2 nuclear spin and 99.8% natural abundance).

According to the nuclear spin value, the theoretical number of lines should be 8 ($2I + 1 = 8$), but experimentally only 4 are recorded. The other four components are not observable because continue in the central part of the spectrum, being covered by another triplet intense spectrum, also stable at room temperature.

It is found that both relative intensities and the width of the four lines are different. This behaviour is perfectly consistent with both the theoretical treatment made by McConnell[10] and the EPR spectra recorded from the solutions of VO^{2+} compounds[6–8].

It must be mentioned that all EPR studies of the existing literature have been performed only for the solutions of the compounds with VO^{2+}. In this study are shown the EPR spectra of $NaVO_3$ in solid state. Since such a study was not performed, we had to use information from the literature regarding the compounds with VO^{2+} in solution.

From Figure 2 were calculated the g factor values and was measured the ΔH_{pp} width (expressed in Gauss) of each line and using Equation (5), were calculated the spin-spin relaxation times T_2, for the two vanadate salts.

The values listed in Table 1 and Table 2 are in the range of 10^{-8}-10^{-9} s, similar to those existing in the literature[9, 14].

Table 1. The spin-spin relaxation times T_2 for the four lines represented in Figure 2(a) Merck

m_I	g	ΔH	$T_2\cdot10^9$ s
- 7/2	2.3169	9.470	6.47
- 5/2	2.1210	11.360	5.45
- 3/2	2.1105	9.470	6.51
- 1/2	2.0960	6.154	10.21

Table 2. The spin-spin relaxation times T_2 for the four lines represented in Figure 2(b) Riedel-de Haën

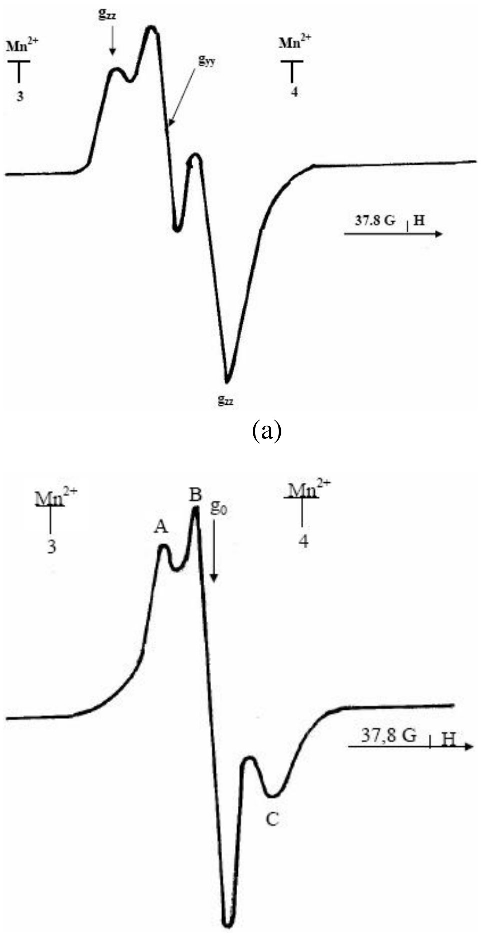
m_I	g	ΔH	$T_2\cdot10^9$ s
- 7/2	2.135	9.470	6.475
- 5/2	2.121	8.990	7.370
- 3/2	2.108	7.570	8.750
- 1/2	2.098	4.735	13.735

Experimentally it is found that $NaVO_3$ provided by different manufacturing companies (Merck and Riedel-de Haën), presents a different spectral and thermal behaviour after irradiation.

From Figure 2 and from Table 1 and Table 2 it is found that although the same substance is irradiated, both the spectra and T_2 relaxation times of the radicals are not absolutely identical. This difference in the radiochemical behaviour is due to the method of preparation of the substance, the existence of various impurities even in a small proportion, the presence of the lattice imperfections and generally, the history of the substance. The four components are well resolved in both vanadates, but some differences were observed both in intensity and line widths, similar behaviour to the EPR spectra of VO^{2+} solutions[15].

The central triplet intensity versus quartet intensity is about 10 times higher in the case of Riedel-de Haën samples and 3-4 times higher in the case of Merck samples. This behaviour shows that the triplet, assigned to the VO (V^{2+}) species, is much larger than that of $V\dot{O}_3$ species.

Heating the samples to the room temperature, after irradiation at 77 K, it is found the rapid decrease of the signals intensity and in the case of $NaVO_3$ Merck, the signal totally disappears after a few hours. Regarding



(a)

(b)

Figure 3. EPR spectrum of Riedel-de Haën NaVO$_3$ powder samples, irradiated at room temperature with a dose of: (a) 4×10^3 Gy; (b) 8×10^3 Gy

NaVO$_3$ Riedel-de Haën irradiated at room temperature, only the triplet formation is found.

In Figure 3 are shown the EPR spectra of the two samples of Riedel-de Haën NaVO$_3$ irradiated with different doses.

The triplet spectra are characterized by the following parameters:

g_{xx}=2.0154±0.0011 g_{yy}=2.0059±0.0001
g_{zz}=1,9931±0.00021 H_{xx}=3211.63 G
H_{yy}=3226.75 G H_{zz}=3247.55 G

The intensity of the three lines varies with the increasing of the irradiation dose. The explanation of this behaviour will be given in the radiolysis mechanism.

3.1 The radiolysis mechanism

The assignment of the EPR signals of the radicals formed in gamma irradiated polycrystalline NaVO$_3$ can also be done based on literature information regarding the irradiation of many oxyanions: Se, Te, Cr, W, Mo[16–20]. The general scheme includes primary reactions of ionization and excitation of VO_3^- ion, followed by secondary reactions of decomposition with oxygen removal and paramagnetic species formation. In the case of NaVO$_3$ these species can be: $\dot{V}O_3$,$\dot{V}O_3^{2-}$, $\dot{O}_2^-$ and $\dot{O}^-$ and lower oxidation states of vanadium, such as: V^{4+}, V^{2+} in the form of VO_2 and VO. The yield of each species depends on many factors: the irradiation conditions, the received dose and mainly, the substance method of synthesis.

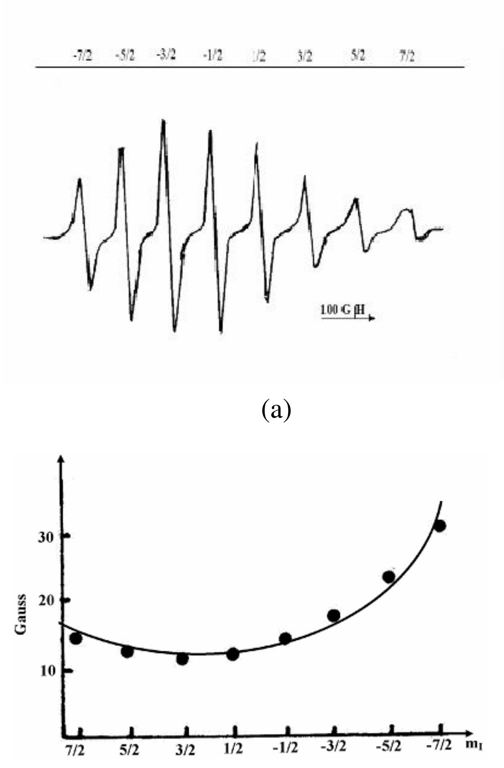
The $\dot{V}O_3$ radical characterizes the formation in the primary process of irradiation of any oxyanion[16–20] and results after the electron removal from the VO_3^- anion. It is a "hole"- type center. The electronic state of vanadium is $3d^5$. The odd electron performs the hyperfine splitting with ^{51}V (I = 7/2) nucleus, natural abundance of 99.8%, which explains the formation of four of the eight hyperfine lines from the EPR spectra. Regarding NaVO$_3$ irradiated in solid state, the $\dot{V}O_3$ radical has thermal stability only at 77 K. The odd electron interaction with the nucleus is even stronger as the oxygen atoms number of the radical is lower[17], because the electron charge density is also distributed on the oxygen atoms. This is the explanation for which the intensity of the 4 recorded lines from $\dot{V}O_3$ is much smaller than that of the VO^{2+} ($3d^1$) ion-radical recorded in solution. The hyperfine structure from VO^{2+} is shown in Figure 4(a) and the line widths in Figure 4(b)[21]. This provided a striking demonstration of the variation in relaxation time for individual nuclear spin state.

The electron line width varies with the vanadium nuclear orientation according to the "microcrystalline" mechanism proposed by Mc Connell[10]. In this mechanism a relatively stable short range order between the transition metal ion and the nearest solvent neighbours was postulated to form "microcrystalls" giving rise to anisotropies in the g-tensor and in the hyperfine interaction tensor. Widths of lines in aquated VO^{2+} with different values nuclear spin quantum number, m_I, differ by as much as 10 G[10].

No simple salts containing V^{4+} have been studied. Most studies of tetravalent vanadium have been made with vanadyl ion (VO^{2+}), which occurs in a number of octahedral complexes[15].

The V atom from VO, resulted from the $VO_3^- \to VO + \dot{O}_2^-$ process, has three unpaired electrons ($3d^3$) and a total spin S=3/2. A state having a total electron spin quantum number equal to 32 is a quartet one, with four components in which the m_s quantum number is allowed to take the values: +3/2, +1/2, -1/2, -3/2. These four states are not usually degenerate over in zero field.

The principal mechanism of the zero field in metal ion



(a)

(b)

Figure 4. (a) The hyperfine spectrum of VO^{2+} in solution of H_2SO_4 (0.01 M) at 30^0C; (b) Line widths versus m_I

arises because of spin-orbit coupling and in these cases can be too large to permit the observation of electron resonance absorption.

The zero field splitting is generally much larger than the hyperfine splittings and EPR spectra are usually interpreted in terms of the spin Hamiltonian containing only Zeeman and zero field terms[5]:

$$\hat{H} = g\beta H\hat{S} + D\left[\hat{S}_z^2 - \frac{1}{3}S(S+1)\right] + E\left(\hat{S}_x^2 - \hat{S}_y^2\right) \tag{6}$$

where, $\hat{S}_x$, $\hat{S}_y$, $\hat{S}_z$, are omponents of the effective spin along the x,y and z axes, D is symmetric tensor called the zero-field splitting tensor (spin-spin coupling tensor)

For an ion V^{2+} with total spin S=3/2 transition $\Delta m_s = \pm 1$ will occur at different fields if is observed at constant frequency. Such multiple transitions are called fine structure following conventional spectroscopic terminology.

If the ion with three unpaired electron (S = 3/2), the fine structure Hamiltonian takes the form:

$$\hat{H} = W_e = D\left[\hat{S}_z^2 - \frac{5}{4}\right] + E\left(\hat{S}_x^2 - \hat{S}_y^2\right) \tag{7}$$

If the ion is axially symmetric, the fine structure constant, E = 0. Entering the Equation (7) in Schrödinger equation ($\Psi = E_n\Psi$) is obtaining Equation (8):

$$\hat{S}_z^2\Psi = \left(\frac{E_n}{D} + \frac{5}{4}\right)\Psi \tag{8}$$

where $\frac{E_n}{D} + \frac{5}{4}$ represents the discrete series of values of the physical entity, represented by the $\hat{S}_z^2$ operator (the own values of the $\hat{S}_z^2$ operator). Regarding V^{2+}, the S_z physical entity has the values: ±1/2 and ±3/2. Under these conditions, S_z^2 has only two values: 1/4 and 9/4. Entering these entities in Equation (8) results Equation (9):

$$E_1/D + 5/4 = 1/4,\ E_1 = -D\, and\, E_1 = +D \tag{9}$$

It results that in zero magnetic field, the energy level has 2D splitting (shown in Figure 5(a)).

When the external magnetic field is applied, a triple EPR line is obtained (having a fine structure) corresponding to the -3/2↔ -1/2, -1/2↔ +1/2, +1/2↔ +3/2 transitions.

In conclusion, the three components (3a, 3b) central spectrum is assigned to VO entity. The lines of this center are more intense than the singlet due to $V\dot{O}_3$ radical, resulted from the primary process of radiolysis ($VO_3^- \rightarrow V\dot{O}_3$+e). This proves that through $NaVO_3$ irradiation, the predominant species is VO.

Experimentally it is found that the B and C lines intensity (Figure 3(a)) of the triplet varies with increasing the irradiation dose. At low doses, below 5×10^2 Gy, the lateral components (A and C) are small compared to the central component B (Figure 3(a)). Increasing the dose of irradiation it is found the decrease of the central line B, simultaneously with increasing of the C component intensity from the right side (Figure 3(b)). This behaviour proves the existence of two radicalic species spectra.

The spectrum of the radical, which overlaps the central triplet (VO), radiolitically formed through irradiation with high doses, belongs most likely to VO^+ ($3d^2$) entity. This entity results from the VO → VO^++e process, formed after accumulation of VO species, previously presented (Figure 5(a)). The VO^+ ($3d^2$) ionic species also presents a fine structure with splitting in zero field, similar to VO. Entering in Equation (6) S = 1, the fine structure Hamiltonian takes the form:

$$\hat{H} = D\left[\hat{S}_z^2 - \frac{2}{3}\right] + E(\hat{S}_x^2 - \hat{S}_y^2) \tag{10}$$

After entering Equation (10) in Schr odinger equation is obtaining:

$$S_z^2\Psi = \left(\frac{E_n}{D} + \frac{2}{3}\right)\Psi \tag{11}$$

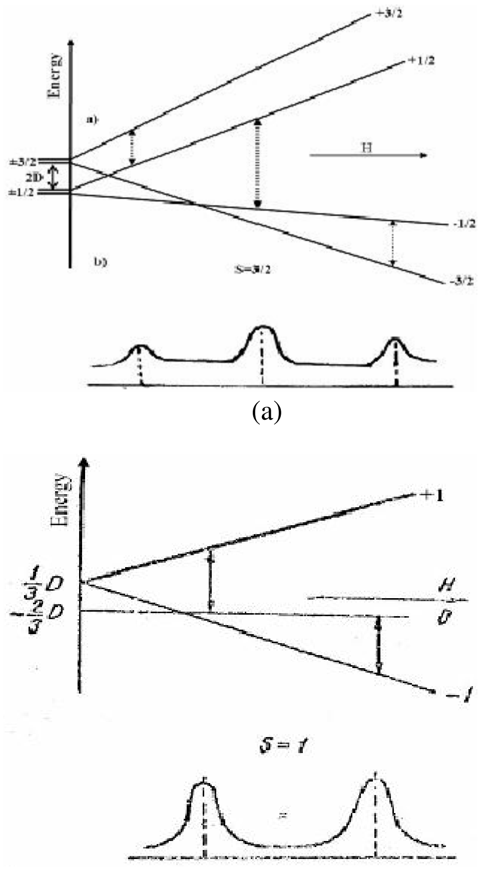


Figure 5. State energies and transitions for a system of spin (a) S=3/2 and (b) S=1 with axial symmetry

In the case of VO^+, the S_z physical entity (z-component of the total spin S = 1) has the values Sz = ±1.0 and S_z^2 = 1.0. Entering S_z^2 in Equation (11) results Equation (12):

$$\frac{E_1}{D}+\frac{2}{3}=1\,E_1=\frac{D}{3}\text{ and }\frac{E_1}{D}+\frac{2}{3}=0\,E_1=-\frac{2}{3}D \qquad (12)$$

Therefore, in zero magnetic field the energy level has D value and when the external magnetic field is applied a double EPR line is obtained, corresponding to (-1)↔ 0, (+1)↔ 0 transitions (Figure 5(b)).

The left doublet component overlaps the central B component of the triplet from Figure 3(b). This means that at high doses this line belongs mainly to VO^+ species. This assignment is also supported by the fact that the A component of the triplet does not change significantly the intensity with increasing the dose. The dose accumulation is shown in Figure 6, for Riedel-de Haën samples irradiation, at room temperature, by representing the central intensity (arbitrary units) versus the absorbed dose.

A rapid increase of EPR signals is seen at low doses.

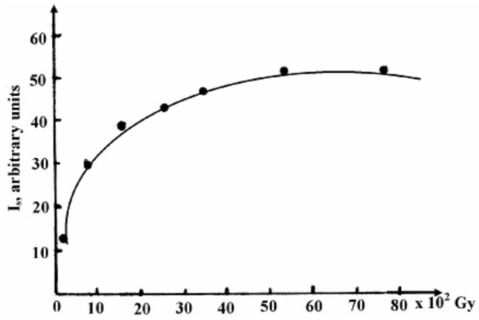


Figure 6. Variation of EPR signal intensity function of integral dose for the gamma irradiated $NaVO_3$ Riedel-de Haën, at room temperature

With increasing the dose of irradiation, a gradually decrease of the intensity is found, having the tendency to reach a plateau. This behaviour proves that the radiolytic process involves not only the formation of VO^+ species from VO, but also their disappearance. The explanation is as follows: the expelled electron from the primary process (e_{sec}) is finally thermalized (e_{term}), after elastic collisions with the molecules. From this state, the electron may either remain trapped in the crystalline lattice, or to be captured by (Na^+, VO^+) cations. In the case of VO_2, resulted from the process, $(VO_3^-)^* \rightarrow VO_2 + \dot{O}^-$, the V atom has a single electron with $3d^1$ configuration (S = 1/2) and the number of the lower levels equal to 2 (2S+1 = 2). This entity has no fine structure because $E_n/D + 1/3S(S+1) = E_n/D + 1/4 = 1/4$. Since $\hat{S}_z^2$ has only one value, equal to 1/4, results that En=0 and D=0.

As noted above, VO_2 has $3d^1$ configuration, similar to VO^{2+}. It is found experimentally a totally different behaviour. If the VO^{2+} ion presents an EPR spectrum having a splitting of 8 lines (Figure 4(a)) due to the odd electron interaction with ^{51}V nucleus, in the case of VO_2 this process does not occur. The only explanation must be attributed to the existence of the two oxygen atoms and the lack of the positive charge, because the charge density of the odd electron is mainly located on the π orbitals of the oxygen. This explanation is also supported by the fact that at 77 K the central component of the triplet is very intense, which proves the overlapping of a singlet from the $\dot{V}O_3$ oxygen atoms.

Through high doses irradiation of a $NaVO_3$ sample at 77 K, the EPR spectrum revealed a large symmetric signal labeled with z, presented in Figure 7.

The singlet has a g value of 0.92526±0.00134 and a line width ΔH_{pp} of 83.1±1.3 G.

The lack of hyperfine splitting suggests a species not couplet with vanadium. A likely candidate would be an oxygen species as $\dot{O}_2^-$ which is known to form easily[22].

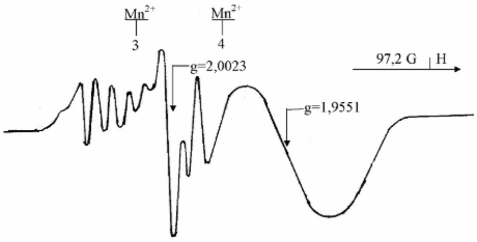


Figure 7. EPR spectrum of $NaVO_3$ Merck polycrystalline sample irradiated at 77 K with a dose of 8×10^3 Gy

We did not observe the signal of $\dot{O}^-$ radical mentioned in the radiolysis mechanism, thus, we consider being most probable for these species to lead at atomic oxygen and electron formation ($O^- \rightarrow O+e$).

The electrons resulted from the previous processes are trapped in the traps of forbidden band of the crystalline lattice. By raising the temperature they are released and they recombine either with a cation or with positive hole with light emission.

4 Conclusions

The radiolysis of gamma irradiated $NaVO_3$ (Merck and Riedel-de Haën) samples in polycrystalline solid state was performed. The EPR spectra indicated the formation of $V\dot{O}_3$, VO, VO^+, $\dot{O}_2^-$, $\dot{O}^-$ species. The EPR spectra of the irradiated samples at 77 K revealed in the case of both substances, the existence of a four components with a fine structure from the interaction of the odd electron $V\dot{O}_3$ radical with ^{51}V nucleus. Spin-spin relaxation times T_2, calculated from the peak to peak line widths, are consistent with those of VO^{2+} radical. In the central part of the spectrum is recorded an intense signal due to the fine structure produced by vanadium from VO and VO^+.

A difference on $NaVO_3$ radiolytic behaviour, determined by the preparation method, was found.

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