EPR OF γ - IRRADIATED CsH$_3$ (SeO$_3$)$_2$

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The γ-irradiated single crystals of trihydroselenite of cesium, CsH$_3$ (SeO$_3$)$_2$, (CTHS) have been studied by method EPR. It was shown that γ irradiation of CTHS produce two type of free radicals – SeO$_2^-$- and O$_2^-$. It was observed the hyperfine and superhyperfine interactions of the magnetic moment of unpaired electron of the radical SeO$_2^-$ with magnetic moments of nuclei ^{77}Se, ^{133}Cs and ^{1}H.

Trihydroselenites of the type MeH$_3$(SeO$_3$)$_2$ (Me=Li, Na, K, Rb, Cs and NH$_4$) belong to class of ferroelectrics with hydrogen bonds (the corresponding crystals will be denoted as LTHS, STHS, KTHS, RTHS, CTHS and ATHS respectively). From this family were investigated by the electron paramagnetic resonance (EPR) method γ-irradiated LTHS (Ivanov & Sergeev, 1974; Edlund & Lund, 1976), STHS (Blinc, Poberaj, Schara & Stepisnik, 1966), KTHS (Sergeev & Falaleev, 1974, Cevc P., Blinc, Srinivasan, Zupancic & Shuvalov, 1980, Machado de Silva, Chaves, Gazzinelli, Ribeiro, Blinc, & Zupancic, 1981) and RTHS (Sergeev & Falaleev, 1975, Yamamoto, Fukui, Abe, Sakai, & Yagi, 1984). In the present work we represent the results of investigation of the free radicals in γ-irradiated CTHS by EPR method.

Single crystals CTHS were prepared by the well known method (Shuvalov, Ivanov, Gordeeva, & Kirpichnikova, 1970). The irradiation of crystals was carried out at room temperature by the dose of ~ 10 Mrad. After irradiation the crystals acquire cherry color. The registration of EPR spectra it was carried out at spectrometer EPR-3 (Institute of Physics, Krasnojarsk).

It was studied the angular dependences of EPR spectra during the rotation of crystal around three reciprocally perpendicular axes x,y,z (axis x and y were selected parallel to crystallographic axes c and b). The accuracy of the installation of the given orientation of a single crystal is evaluated as 1^0.

Spectra EPR consist of eight equidistant central lines and single sideline with g-factor strongly different from g-factor (g$_e$) of free electron (Fig.1). The half-width of this line is ~ 30 G, while the half-widths of the central components are ~2,5 G. The significant deviation of the g-factor of this line from g$_e$ and its high half-width indicate that this line is caused by the radical, whose ground state contains the significant admixture of the orbital angular momentum (Atkins & Symons, 1967).

The registration of EPR spectra at large amplification made it possible to observed at some crystal orientations the additional weak spectral lines (Fig.2).
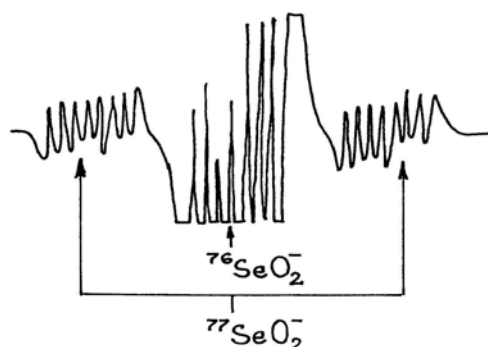

Fig.2. Hyperfine and superhyperfine structure of EPR spectrum of γ-irradiated CTHS

Fig.1. Typical spectrum EPR of γ-irradiated CTHS.

These weak lines are located symmetrically relative to the center of intensive lines. Also, as central intensive lines, additional lines form groups of eight equidistant components with the splittings between them, which coincide with the splittings between the lines of the intensive central part of the spectrum. The ratio of the intensities of the additional and central lines ~10% coincides with the isotopic abundance of nuclei Se. This fact allows to assume that the central part of the spectrum is caused by the radicals, which contain the nonmagnetic isotope [76]Se (natural abundance ~ 92%), and additional weak sidelines are caused by the hyperfine interaction (HF) of unpaired electron with the magnetic moment of nucleus [77]Se (spin I = 1/2, natural abundance ~ 8%).

The analysis of the angular dependences of EPR lines showed that all eight equidistant central lines behave as unified whole. This is simple to explain, if one assumes that the appearance of these eight lines is caused by superhyperfine interaction (SHF) of the unpaired electron with the magnetic moment of nucleus [133]Cs (spin I = 7/2, natural abundance - 100%). SHF interaction with the magnetic moment of nucleus [133]Cs is approximately isotropic with the constant ~ 10 G. So from our data it follows that the γ irradiation of CTHS produce two type of radicals, We will denote their as radical I and radical II.

The angular dependence of EPR spectrum of the radical I may be describe by spin-hamiltonian

$$H_I = \mu_B \vec{S}\vec{\vec{g}}_I\vec{B} \ , \qquad (1)$$

where $\vec{\vec{g}}_I$ - tensor of g-factor, $\vec{S}$ - spin of electron, μ_B is of Bohr magneton.

The angular dependence of EPR spectrum of the radical II may be describe by spin-hamiltonian

$$H_{II} = \mu_B \vec{S}\vec{\vec{g}}_{II}\vec{B} + \vec{S}\left(\vec{\vec{A}}_1\vec{I}_1 + \vec{\vec{A}}_2\vec{I}_2\right), \qquad (2)$$

where $\vec{\vec{A}}_1$ and $\vec{\vec{A}}_2$ are the tensors of HF interaction and SHF interaction with magnetic moments of nuclei [77]Se and [133]Cs, $\vec{I}_1$ and $\vec{I}_2$ are the spins of nuclei [77]Se and [133]Cs nuclei, correspondingly.

The major values and directional cosines of the g-tensors of free radicals I and II are represented in the Table. The determinations of the principal values and directional cosines of the HF interaction tensor with magnetic moment of nucleus [77]Se are very difficult because of their strong overlapping with the intensive central lines.

Free radical I.
The obtained principal values of g-tensor for this

radical very well agree with the expected values for the free radicals O_2^- (Atkins & Symons, 1967). It should be note that this radical was not observed early not in one of the investigated by the method EPR of γ-irradiated trihydroselenites.

The free radical O_2^- is the ionized form of the molecular oxygen (Atkins & Symons, 1967). It is the 17-electronic variety of the π-type radical with the symmetry $D_{\infty h}$ (Fig..3).
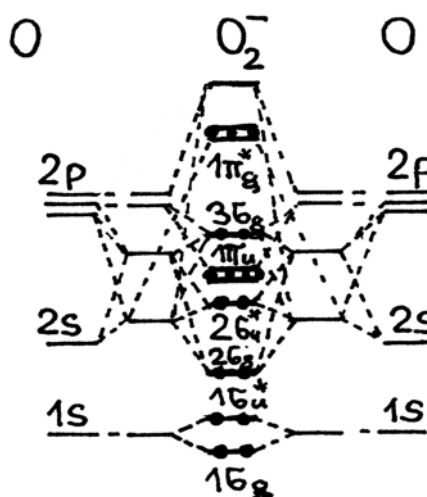

Fig.3. Diagram of the energy levels of free radical O_2^-.

Seventeen electrons of free radical O_2^- are arranged so that unpaired electron occupies one of the nonbonding π - orbitals (Fig.3).
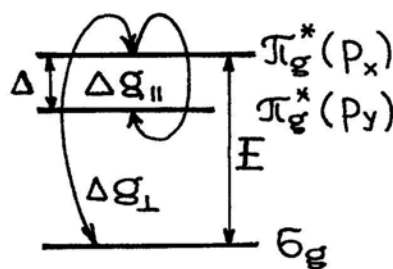

Fig.4. Excitations, which determine the deviations of $g_{zz}=g_{\parallel}$ and g_{xx}, g_{yy} ($g_{\perp}$) from g_e.

The large contribution of orbital angular momentum to the total momentum of unpaired electron leads to very strong coupling of the electron magnetic moment with crystal lattice. This results to the very short spin-relaxation time of free radical O_2^-, by which the strong broadening of EPR spectrum of this radical is caused (Atkins & Symons, 1967). Therefore frequently in the

case of linear radicals a signal EPR is not observed at room temperature and g-factor considerably differs from g_e. From the fact, that spectra EPR from the linear radical O_2^- are observed at room temperature in γ-irradiated CTS, it follows that orbital angular momentum is "frozen" by crystalline field. The asymmetric environment of free radical O_2^- removes degeneration of $\pi_g^*(p_x)$ and $\pi_g^*(p_y)$ orbitals (fig.4) and in the first approximation, unpaired electron localized on one of them. The excited configuration corresponds to the passage of the coupled electron from $\pi_g^*(p_y)$ - level to $\pi_g^*(p_x)$ - level. Close arrangement of these levels

(Fig.4) leads to the strong mixing of these states because of the spin-orbit interaction. This leads to the high deviation of g_{zz}-component of g-factor tensor (axis z is parallel to direction O-O) from the value g_e. The greatest contribution to the deviation g_{xx} and g_{yy} from g_e gives the excited configuration, obtained upon transfer of the electron from σ_g level to the level $\pi_g^*(p_x,p_y)$. It leads to deviations of g_{xx} and g_{yy} from g_e much smaller than deviation of g_{zz} from g_e. So the characteristic property of free radical O_2^- is high value of one of major component (g_{zz}) of g-tensor, whose the principle direction coincides with oxide atoms bonding.

Table. The principle values and directional cosines of the g-tensors of free radicals O_2^- and SeO_2^- in γ-irradiated CTHS

Free radical	Principle values	Directional cosines		
		x	y	z
I (O_2^-)	$g_{xx}=2,096 \pm 0,005$	0,991	-0,005	-0,135
	$g_{yy}=2,189 \pm 0,005$	0,062	0,905	0,421
	$g_{zz}=1,980 \pm 0,005$	0,121	-0,426	0,897
II (SeO_2^-)	$g_{xx}=2,014 \pm 0,005$	O,883	-0,219	0,415
	$g_{yy}=2,031 \pm 0,005$	0,365	0,875	-0,317
	$g_{zz}=1,994 \pm 0,005$	-0,294	0,432	0,853

Free radical II.

The obtained principal values of g-tensor for free radical II very well agree with the expected values for the free radicals SeO_2^- (Atkins & Symons, 1967). In the previously investigated trihydroselenites by EPR method it was shown that γ irradiation also leads to the formation of free radicals SeO_2^-.

Interesting peculiarity of EPR spectra of CTHS is the superhyperfine structure of spectra, caused by superhyperfine interaction of the magnetic moment of unpaired electron of radical SeO_2 with the magnetic moment of nucleus ^{133}Cs. The appearance of electron spin density on the nucleus ^{133}Cs can be explained by effect of the overlapping of the wave function of unpaired electron of free radical SeO_2^- with the wave functions of cation Cs^+, which has a greatest from all alkali metals the ionic radius of Cs^+ (Coulson, 1961).

In conclusion we note also the interesting peculiarity of EPR spectra of free radical SeO_2^- in γ-irradiated CTHS. At the orientation of magnetic field B $(1/\sqrt{3}, 1/\sqrt{3}, 1/\sqrt{3})$ it is observed spectrum EPR, which consists sixteen lines (Fig.5) The presence of sixteen lines in the spectrum EPR can be explained by superhyperfine interaction of unpaired electron of the free radicals SeO_2^- with the magnetic moment of atomic nucleus of hydrogen. Similar superhyperfine interaction was earlier observed in γ-irradiated LTHS (Ivanov & Sergeev, 1974, Edlund & Lund, 1976) and KTHS (Sergeev & Falaleev, 1974). For the purpose of the proof of this assumption we investigated the spectra EPR of γ-irradiated trideuteroselenite of cesium (CTDS) (Fig.5), in which hydrogen atoms were substitutes for the atoms of deuterons.

From the comparison of EPR spectra of γ-irradiated CTHS and CTDS (Fig.5) it follows that the replacement in CTHS of hydrogen atoms to the atoms of deuterium leads to the disappearance of additional splitting of EPR spectral lines.
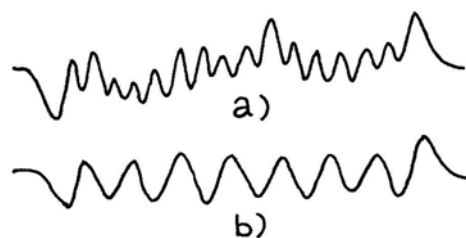

Fig.5. Spectra EPR of γ-irradiated CTHS (a) and CTDS (b) at the orientation of magnetic field B $(1/\sqrt{3}, 1/\sqrt{3}, 1/\sqrt{3})$

This unambiguously proves, that additional splitting of spectrum EPR observed in γ- irradiated CTHS is caused by superhyperfine interaction of the magnetic moment of the unpaired electron of free radical SeO_2^- with the magnetic moment of the atomic nucleus of hydrogen.

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