



EPR STUDY OF PARAMAGNETIC CENTERS IN GAMMA IRRADIATED POLYCRYSTALLINE AMMONIUM PARAMOLYBDATE (APMO) AND AMMONIUM PARAWOLFRAMATE (APW)

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Received June 9, 2011

The paramagnetic centers produced by gamma irradiation at 77 K and room temperature in the polycrystalline ammonium paramolybdate $\text{Mo}_7\text{O}_{24}(\text{NH}_4)_6 \cdot 4\text{H}_2\text{O}$ (APMo) and ammonium parawolframate $\text{W}_5\text{O}_{17}(\text{NH}_4)_4 \cdot 2,5\text{H}_2\text{O}$ (APW) were studied by EPR spectroscopy. The EPR spectra were assigned to the NH_3^+ radicals, with Mo (V), for ammonium paramolybdate (APMo) and $[\text{W}_5\text{O}_{17}]^{3-}$, with W (V), for ammonium parawolframate (APW). A mechanism for the radiolytic process was developed.

INTRODUCTION

The investigation by EPR technique of the irradiated inorganic compounds leads to interesting results concerning both the nature of paramagnetic centers formed, and the thermal stability and their mode of disappearance.

The ammonium salts of the oxyanions irradiated with γ and X rays exhibit a specific behavior compared with the salts of other cations.

By γ irradiation of the $\text{NH}_4\text{H}_2\text{AsO}_4$ monocrystals, in the EPR spectra, the existence of the NH_3^+ radical has been identified.¹ The radiolysis products of the NH_4^+ ion contribute to the reduction of arsenate ion.

The $(\text{NH}_4)_2\text{SeO}_4$ radiolysis form three radicalic species: SeO_4^- , SeO_3^- , SeO_2^- . In the

central part of the EPR spectrum additional lines are observed, which have been assigned to the radicals derived from the ammonium ion.²

The radiolytically formed species, from NH_4^+ , resulted from polycrystalline $(\text{NH}_4)_2\text{CrO}_4$ irradiation perform the reduction of the chromate anion in CrO_3^- and CrO_2^- radicals.³

Analyzing the paramagnetic centers produced by the NH_4Cl irradiation, Cole⁴ recorded at room temperature an EPR spectrum equally spaced, having the relative intensity of the lines 1:3:3:1, assigned to the NH_3^+ radical ion.

The EPR study of gamma irradiated single crystals of $(\text{NH}_4)_2\text{SO}_4$ at room temperature revealed the existence of the NH_3^+ radicals resulted from NH_4^+ .⁵

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EXPERIMENTAL

The irradiations were performed at room temperature in open ampoules and at liquid nitrogen temperature in closed ampoules, using a ^{137}Cs source with $3,2 \cdot 10^{13}$ Bq activity and $1,05 \cdot 10^2$ Gyh $^{-1}$ dose rate.

Ammonium paramolybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ with p.a purity from Riedel de Haen and ammonium parawolframate $(\text{NH}_4)_4\text{W}_5\text{O}_{17} \cdot 2,5\text{H}_2\text{O}$ with p.a purity from Merck have been used to prepare the samples.

The EPR spectra of the irradiated samples were recorded with an ART 6 spectrograph (IFIN Magurele), operating in the X band, with a 100 kHz high frequency modulation. Mn^{2+} ion in *CaO* matrix, as a standard was used to determine the g factor.

RESULTS AND DISCUSSION

a) The radiolysis study of ammonium paramolybdate

Molybdenum (Mo), element of 4d transition group, has been less studied by EPR as oxycompounds.⁶⁻⁹

The Mo oxygenated compounds, such molibdates and paramolibdates type, where Mo is in the VI valence state, are non paramagnetic but through irradiation with X, β , and neutron radiations lead to paramagnetic centers with Mo in V ($4d^1$) valence state, which remain trapped in the crystalline network and can be studied by EPR. It is important to note, that in the case of these substances, as in the case of the other Cr and W oxyanions, differences were found in the radiosensitivity of the salts, depending on the cation nature. The radiolytic behavior of the ammonium salts is different from the corresponding one of the alkali and alkaline earth salts.

The EPR studies performed on these irradiated systems¹⁰ allowed to obtain information on both the structure and the nature of the chemical bonds.

By *APMo* irradiation, in polycrystalline state at 300 K, radicalic species having complex spectra are formed. In Fig. 1 is illustrated a spectrum obtained after *APMo* irradiation with a dose of $1,3 \cdot 10^4$ Gy.

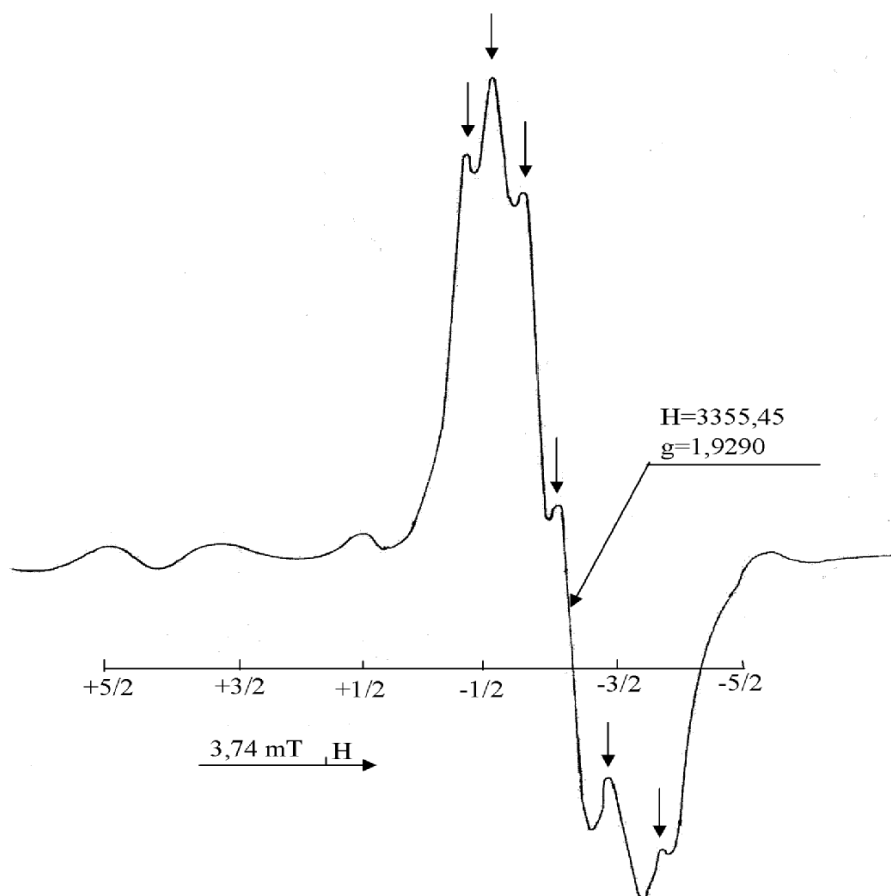


Fig. 1 – The EPR spectrum of polycrystalline *APMo* γ irradiated at room temperature with a $1,3 \cdot 10^4$ Gy dose.

In the center of the spectrum, an intense singlet signal due to the even isotopes ($I = 0$) of Mo having the mass number 92, 94, 96, 98, 100 (natural abundance 74.85%) is observed. A hyperfine structure overlaps this signal with six components of low intensity, which comes from the Mo odd isotopes ($I = 5/2$), namely: ^{95}Mo (natural abundance 15.7%) and ^{97}Mo (natural abundance 9.45%).

Nuclear spins of the two isotopes (^{95}Mo and ^{97}Mo) are equal ($I = 5/2$) and the magnetic moments are very close $\mu_{95\text{Mo}} = -0.9099 \mu_r$, $\mu_{97\text{Mo}} = -0.9290 \mu_r$.

Interpretation of the spectra from each one isotope is difficult, due to the fact that they overlap, leading to the hyperfine structure alteration.

The spectrum, being almost isotropic, can be described using a spin hamiltonian of the form:

$$\hat{H} = g\beta H_0 S_z + a(\hat{I}_x \hat{S}_x + \hat{I}_y \hat{S}_y + \hat{I}_z \hat{S}_z) \quad (1)$$

with: $S = 1/2$ and $I = 0$ for the even isotopes (74,85%)

$S = 1/2$ and $I = 5/2$ for the odd isotopes of Mo (25,15%)

$g = 1,9290 \pm 0,003$; $a = (4,301 \pm 0,1) \text{ mT}$

These values of the spectral parameters are comparable with those obtained from MoOCl_3 .¹¹
 $g = 1,949 \pm 0,002$, $a = (5,24 \pm 0,1) \text{ mT}$.

From Fig. 1 it is noted that the singlet signal is splitted into six components with a hyperfine constant $a = (1,306 \pm 0,2) \text{ mT}$. This additional splitting on the central component, which is well resolved, is due to the interaction with a nucleus with the spin $I = 5/2$.

From information provided by the structure of the EPR spectra, is concluded that the Mo (V) radical, formed by irradiation, interacts with one of the odd isotopes ($I = 5/2$) of Mo (VI), covalently linked. This hypothesis assumes for the *APMo* structure, the existence of a central Mo (VI) atom, which binds to other six Mo atoms, including those reduced after irradiation.

The information obtained from the EPR spectra is a confirmation concerning the chemical structure of this compound as an ISOPOLY-ACID ammonium salt, with $[\text{Mo}(\text{MoO}_4)_6](\text{NH}_4)_6$ formula, in which an atom of Mo (VI) is the central atom octahedrally surrounded by 6 MoO_4^{2-} groups.¹²

The formation of Mo (V), in the irradiated samples, was also revealed by radiochemical separation of Mo (V) from Mo (VI).¹³

Similar spectra to the one presented in Fig. 2 were obtained for the γ irradiated samples with a 10^4 Gy dose at 77 K and recorded at the same temperature.

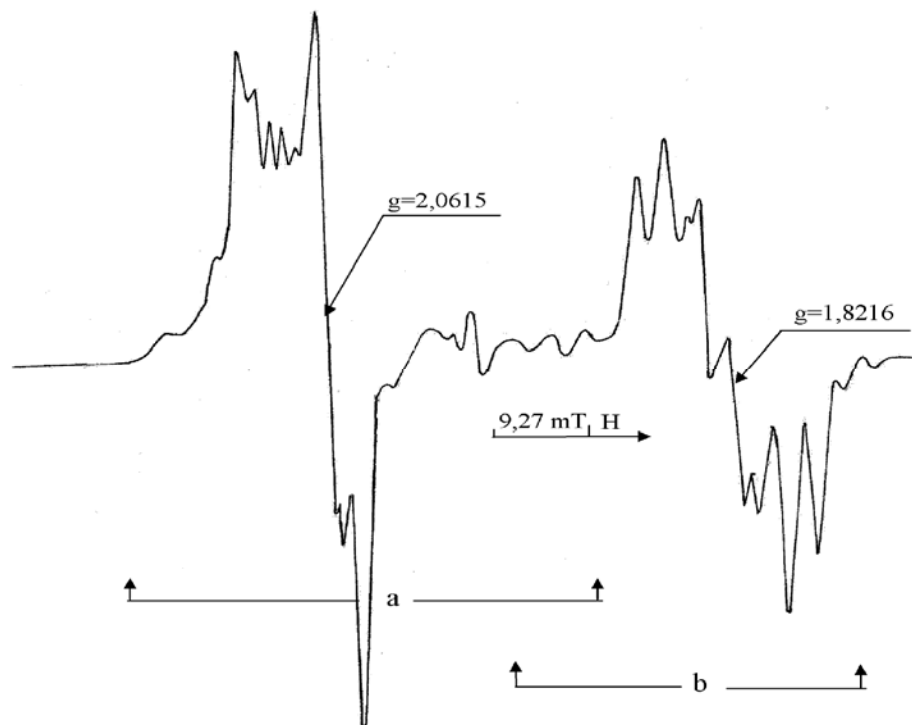


Fig. 2 – The EPR spectrum of APMo polycrystalline sample irradiated with a 10^4 Gy dose at 77 K.

The spectrum from Fig. 2 is more complex than that obtained by irradiation at room temperature, because besides the (2b) signal of the radicalic species with Mo (V) at a high field ($g = 1,8216$), similar to that from Fig. 1, the (2a) signal is recorded, at a lower field ($g = 2,0615$) having 12 components. Based on the spectral parameters,⁴ this structure was assigned to the NH_3^+ radical,

formed by NH_4^+ irradiation. The radical spectrum of NH_3^+ , resulted by NH_4^+ irradiation is due to the hyperfine interaction of the odd electron with the magnetic moment of the ^{14}N nucleus with the spin $I = 1$ and with three equivalent H nuclei ($I = 1/2$). The theoretical hyperfine structure of this spectrum is presented in Fig. 3.

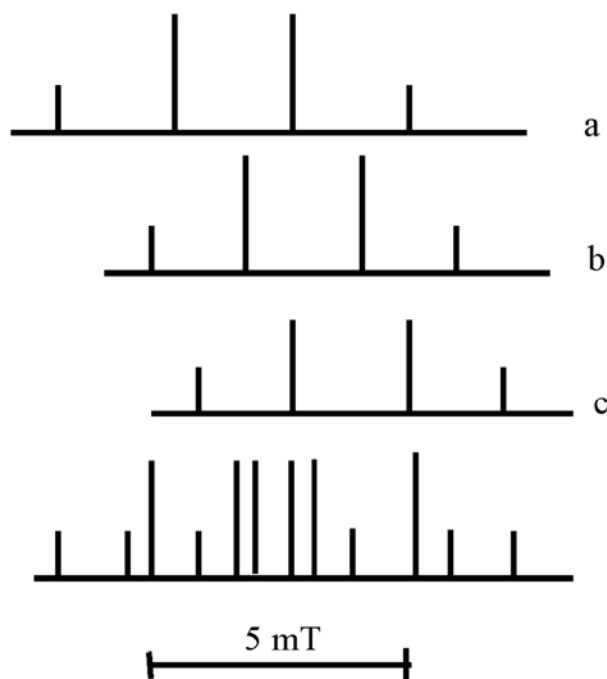


Fig. 3 – NH_3^+ radical spectrum resulted from a triplet of quartets.

The odd electron interaction with the nucleus of the nitrogen atom, splits the spectrum in three equal lines (a, b, c) both as the intensity and the spacing, and the interaction with the three equivalents protons produces the splitting of each line into four components equally spaced, having the relative intensity 1:3:3:1. Finally a triplet of quartets is formed, respectively, a spectrum with 12 components, similar with that highlighted at the NH_4Cl irradiation.⁴

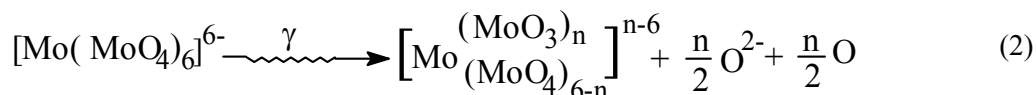
It should be specified that this signal was not observed in the samples irradiated at room temperature, but neither in those irradiated at 77K and recorded at room temperature, which proves

that the NH_3^+ radical is stable only at low temperature.

In conclusion, NH_3^+ and Mo (V) radicals are formed only by $APMo$ irradiation, at liquid nitrogen temperature.

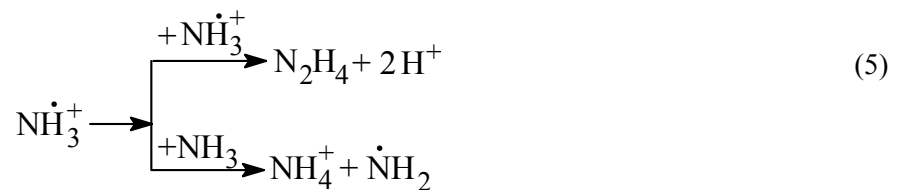
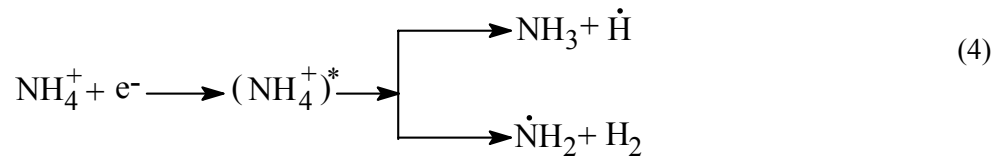
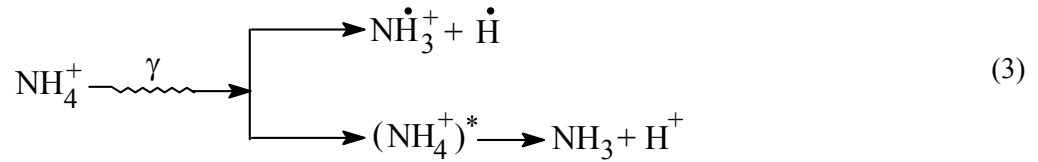
There are two possibilities concerning the formation mechanism of the paramagnetic species having Mo in V valence state.¹⁴

One of them consists in the reduction performed by γ radiations to some MoO_4^{2-} anions, directly linked to central Mo (VI), a chemical process in full compliance with the 6 components hyperfine structure of the EPR spectrum from Fig. 1.



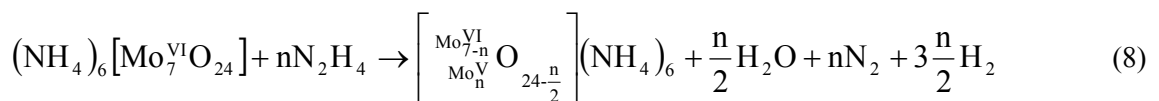
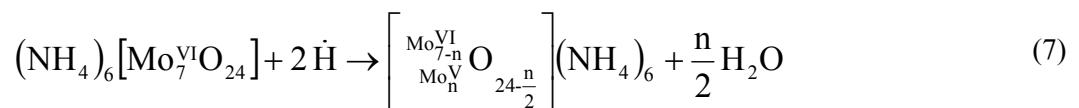
The radical species containing Mo (V) may derive from molybdate oxyanion reduction by $\dot{N}H_2$, \dot{H} , $N_2\dot{H}_4$ reducing groups, radiolytically

formed from NH_4^+ , by the following possible reactions:



The N_2H_4 formation, in the radiolysis process of some ammonium salts was highlighted by Koksal and Yavuz¹⁵ using EPR technique.

The reducing process performed by \dot{H} and $N_2\dot{H}_4$, can be represented as:



The EPR signal intensity dependence of the time of irradiation is shown in Fig. 4.

It was ascertained a radical concentration increase with increasing irradiation dose followed by reaching a maximum (Fig. 4). This behavior is explained by the fact that besides the formation process of Mo(V) radicals through the reduction process with \dot{H} and hydrazine, also a process of oxidation to Mo(VI) in air takes place.

b) The radiolysis study of ammonium parawolframate

Tungsten (W) is a transition element from 5d platinum group. In the literature there are few papers concerning W (VI) compounds, irradiated with ionizing radiations and studied by EPR.¹⁶⁻¹⁷ As in the case of *APMo*, the radiolytical behavior of *APW* differs from that corresponding to other salts.

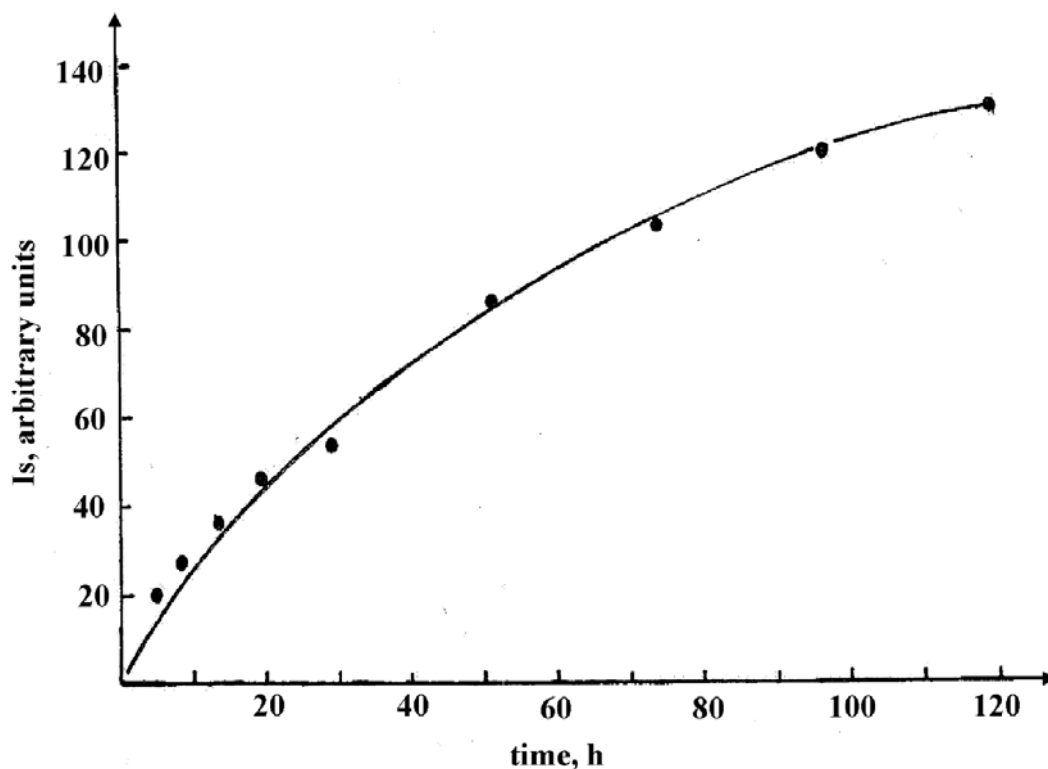


Fig. 4 – The EPR signal intensity variation of an *APMo* polycrystalline sample γ irradiated at room temperature, versus time (dose rate $1,05 \cdot 10^2 \text{ Gyh}^{-1}$).

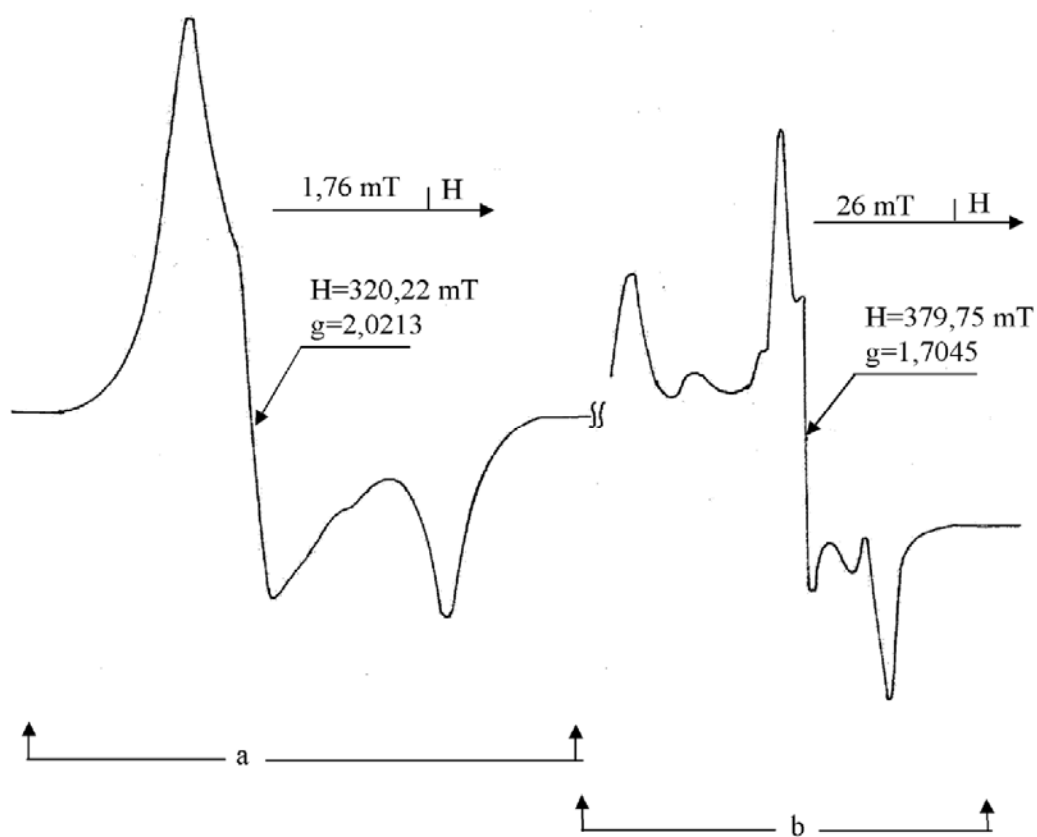
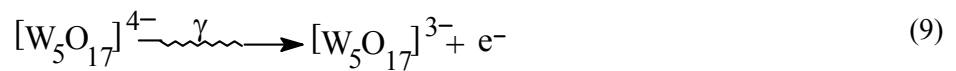


Fig. 5 – The EPR spectrum of polycrystalline $(\text{NH}_4)_4\text{W}_5\text{O}_{17} \cdot 2.5\text{H}_2\text{O}$ irradiated at 77K with a dose of $2,8 \cdot 10^3 \text{ Gy}$, recorded at the same temperature.

In the present study the paramagnetic centers formed on *APW* irradiation were investigated. The chemical formula of *APW* is $(NH_4)_4W_5O_{17} \cdot 2.5H_2O$.

APW, with W (VI), irradiated in polycrystalline state at 77 K presents complex EPR spectra. The spectrum analysis suggest the existence of two sets of lines marked with a and b, as shown in Fig. 5.

The 5a spectrum is presented as an asymmetric signal with $g_{\parallel} < g_{\perp}$, respectively $g_{\parallel} = 2,0033 \pm 0,0007$, $g_{\perp} = 2,0275 \pm 0,0007$ and a width of $\Delta H_{pp} = 3,84$ mT.



The spectrum from Fig. 5b is also asymmetrical and belongs to a radical species that is unstable at room temperature and has a lower intensity than 5a spectrum. The existence of the hyperfine splitting and the spectral characteristics suggest that the radical coming from a paramagnetic species, in which the odd electron interacts with the nuclear spin of W (I=1/2), producing the corresponding hyperfine structure.

The intense central line comes from the even isotopes of W having the mass number 180, 182,

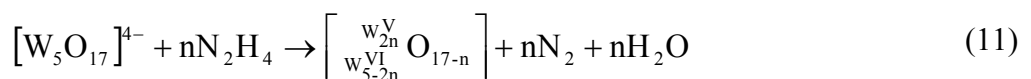
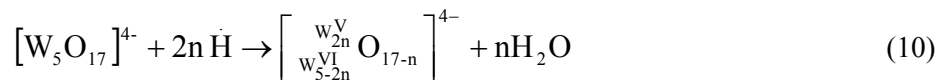
It is noted that the corresponding radical has the value of g factor greater than the free electron one and is unstable with increasing temperature (it disappears at room temperature).

This signal is attributed to radiolytically formed $[W_5O_{17}]^{3-}$ radical, following the expulsion of one electron from para-wolframic anion. The $[W_5O_{17}]^{3-}$ radical is similar with the radicals having deficit of electrons, observed for the *CaWO₄* and *BaWO₄* irradiation.¹⁸

184, 186, natural abundance 85,6%, and the hyperfine structure of low intensity from the odd isotopes (I=1/2) of ¹⁸³W (14,4% abundance).

This signal is attributed to a paramagnetic species containing W in V valence state. Its formation is explained by reduction from VI to V valence state in presence of H atoms reducing fragments derived from radiolysis, from NH_4^+ group which occurs during irradiation.

The reducing process can be thus represented:



This process is common to all irradiated salts containing NH_4^+ group.

The producing possibility of the previous reaction is supported by the fact that in the irradiated samples at 77 K, the resonance of H atoms, trapped in the crystalline network, is not found.

An argument to support the H atoms involving in the reducing mechanism of the parawolframate ion is the following experiment: it was performed the *APW* irradiation with UV radiations emitted by a mercury lamp (HBO500) for 5 hours at 77 K.

The EPR spectrum from Fig. 6, belonging to H atoms, disappears after bringing the sample for 10 seconds at room temperature.

To prove the involvement of the reducing species in W (V) radical formation, were also irradiated oxycompounds having W (VI), which do not contain the NH_4^+ ion.

By $Na_2WO_4 \cdot 2H_2O$ gamma irradiation, in polycrystalline state, at 77 K, in the same condition as in the case of *APW*, the formation of W (V) radical in the EPR spectra was not revealed. Constantinescu *et al.*¹⁹ has analyzed by mass spectrometry the gaseous products formed by the irradiation of *APW* vacuum samples and found the existence of some atoms and simple molecules containing hydrogen and nitrogen, confirming the formation of the reducing species, by the action of radiations upon NH_4^+ ion.

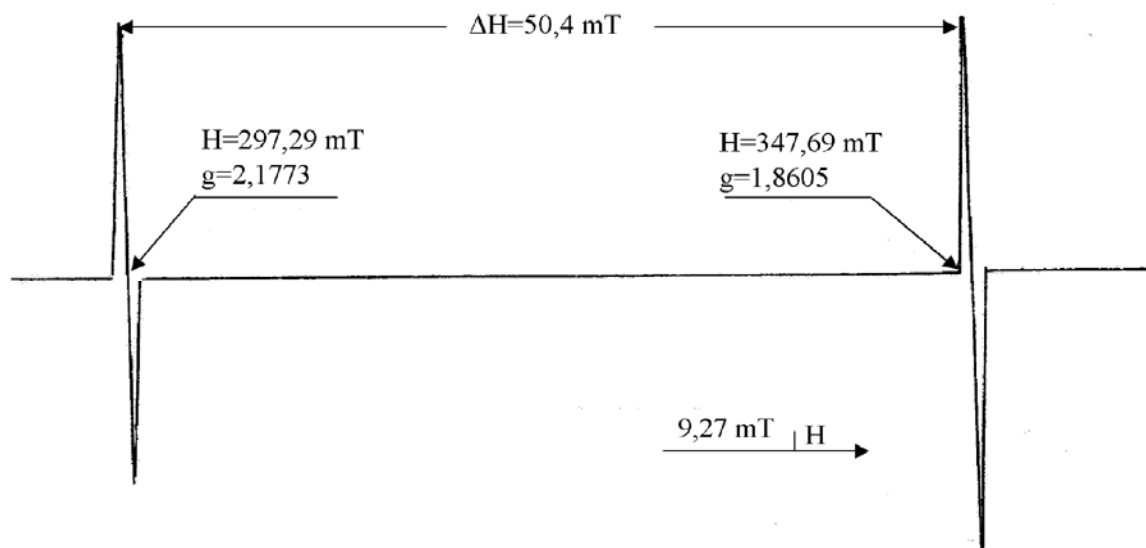


Fig. 6 – EPR spectrum of the H atoms, formed by APW irradiation with UV radiations at 77 K.

The different radiolytic behavior of the ammonium salts is determined by the concrete structure of the crystalline lattice. Thus, if for the NH_4ClO_4 irradiation,²⁰ the NH_3^+ radical is also stable at room temperature, for the NH_4Cl ²¹ and APMo irradiation, this radical is stable only at 77 K.

Moreover, by $5(\text{NH}_4)_2\text{12WO}_3 \cdot 5\text{H}_2\text{O}$ irradiation at 77 K,¹⁹ the NH_3^+ radiolytic formation was highlighted, in the EPR spectrum, as in the case of APMo, but the present study shows that for $(\text{NH}_4)_4\text{W}_5\text{O}_{17} \cdot 2,5\text{H}_2\text{O}$ irradiation, the existence of this paramagnetic species is not observed.

CONCLUSIONS

The study of the paramagnetic centers produced on gamma irradiation of polycrystalline $\text{Mo}_7\text{O}_{24}(\text{NH}_4)_6 \cdot 4\text{H}_2\text{O}$ at 77K and room temperature was performed. The recorded spectra were assigned to the NH_3^+ radicals and to Mo (V) resulted through Mo (VI) reduction in the irradiation process.

The EPR spectra, recorded from $\text{W}_5\text{O}_{17}(\text{NH}_4)_4 \cdot 2,5\text{H}_2\text{O}$, irradiated at 77 K, suggested the formation of two paramagnetic species assigned to $[\text{W}_5\text{O}_{17}]^{3-}$ and W (V) radicals, stable only at this temperature. A radiolytic scheme was proposed.

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