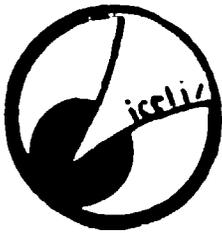
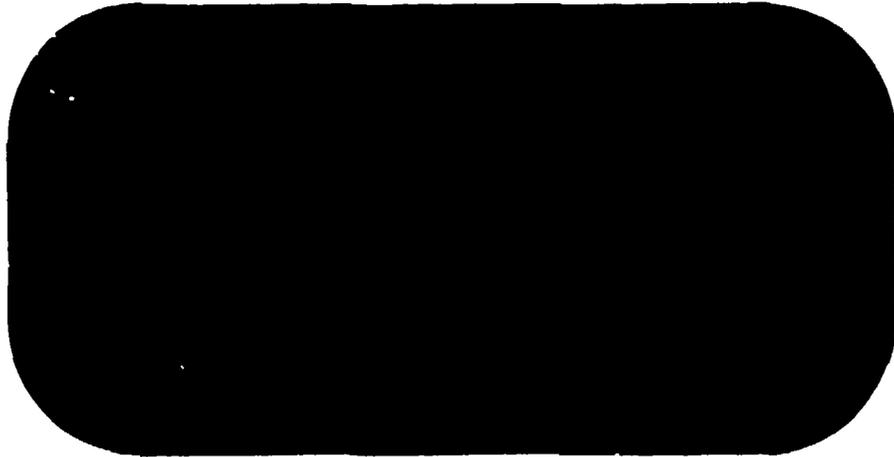


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EPR spectra of some irradiated

polycrystalline perrhenate

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Abstract : An EPR study of the paramagnetic centers formed by γ , electron and neutron irradiation of the NaReO_4 and KReO_4 was made. In the EPR spectra of the powder samples irradiated γ , with electrons and neutrons, the presence of three types of paramagnetic centers was observed. From the EPR parameters, the centers were attributed to the ReO_4^\bullet , ReO_3^\bullet and ReO_2^\bullet radicals respectively. The lower intensity of the spectra observed by KReO_4 samples irradiation showed a higher radioresistance of the KReO_4 than that of NaReO_4 . A radiolitical scheme taking into account the paramagnetic centers formation was proposed.

INTRODUCTION

The chemical forms of radorhenium produced by irradiation with high energy protons have been previously investigated by chemical methods by one of the authors /1,2/, showing the influence of the chemical environment on the behaviour of Re recoil nuclei and also the presence of some reduction and oxydation processes in the thermal annealing.

Inasmuch the chemical methods are not free of secondary effects due to the fact that the samples solvation can frequently lead to chemical modifications, one tried to performe studies on these systems also by physical methods without destroying the solid phase which was irradiated. Such a study on these systems irradiated with neutrons was made by angular correlations /3/ which put into evidence the existence of strong perturbations of magnetic and electric origin. Since the defects produced by irradiation (which plays an important role in the behaviour observed) are in great measure paramagnetic, we considered interesting to study these irradiated systems also by EPR, another non-destructive method which proved to be very useful to the study of paramagnetic defects formed in irradiation processes.

In the present work we tried to made an EPR study of paramagnetic centers formed by the irradiation of polycrystalline NaReO_4 and KReO_4 , following their formation, stability and recombination.

EXPERIMENTAL

Materials

NaReO₄ was prepared as previously reported / 1/ and KReO₄ was reagent - grade.

Irradiations

Gamma, electron and neutron irradiations were effected. The samples were γ irradiated using two ⁶⁰Co sources, one of 5000 Ci of a piscine type and the other of 16.000 Ci of Gammacell type. The irradiations were effected at liquid nitrogen temperature and afterwards the samples were transferred into the spectrograph cavity and examined at the same temperature.

The irradiations with electrons (E = 3 MeV) were effected at room temperature with the linear accelerator of Central Institute of Physics - Bucharest. To be mentioned that for avoid the samples heating, an air jet was passed over the samples during irradiation.

Neutron irradiations were effected in VVR-S reactor of CNF - Bucharest, using fluxes of 10^{11} - 10^{12} n/cm².s.

EPR measurements

EPR spectra were recorded using an EPR spectrograph, which operates in X-band, having the magnetic field modulated in high frequency (100 KHz). For the g-values determination, Mn²⁺ and peroxyamine-disulphonate were used as standard. EPR spectra were recorded at room temperature, at 77 K and also at different temperatures in the range -196°C and 200°C using a device for variable temperatures.

RESULTS

NaReO_4 . Samples of polycrystalline NaReO_4 powder were γ irradiated with ^{60}Co source having an activity of 16000 Ci with integral doses of about 10^6 rad., the rate dose being of $1,15 \times 10^6$ rad/h. EPR spectra recorded at 77 K, present a central asymmetric intense signal (A) which has on both side lines of very low intensity. (B and C) (Fig.1).

By heating step by step the samples irradiated in the above conditions up to room temperature, we observed that the central signal noted A decreases, at room temperature having an intensity comparable with that of the side signals, the intensity of which did not change in this range of temperature. In view to observe how change the form and intensity of the central line of the spectrum by annealing, NaReO_4 samples were heated directly in the resonance cavity for 10 minutes every 20 degrees, recording EPR spectra after every heating (Fig.2).

One observes that the intensity of central signal (A) decreases without variation in the form of the line. The isochrone variation of signal intensity versus the temperature at which the sample was heated, is shown in Fig.3.

The straight line obtained suggests that there is only one recombination process and the signal A belongs only to one type of paramagnetic centers. This signal is characteristic for a radical with $g_{zz} \neq g_{yy} = g_{xx}$. The assignment for the g-values was made in accordance with Kneubühl /4/ and we obtained :

$g_{\parallel} = 2.0093 \pm 0.0005$, $g_{\perp} = 2.0025 \pm 0.0005$. No hyperfine structure was observed.

NaReO_4 powder was also γ irradiated with smaller doses

using ^{60}Co source of 5000 Ci. In this case, EPR spectrum is of lower intensity but having a similar form with that obtained by irradiation with high doses. The only difference is that the intensity of A signal being smaller, one observes better the signal B. The heating up to room temperature of the samples irradiated at 77K leads to the diminution of the A signal intensity, remaining a signal similar with that obtained in the samples γ irradiated with high doses.

The polycrystalline powder of NaReO_4 was also irradiated with 3 MeV electrons at room temperature with doses in the range of 10^7 rad. In Fig.4 is given the spectrum recorded at the room temperature on the samples irradiated with an integral dose of 22 Mrad.

Inasmuch the spectrum seems to be more complex in this case, we tried to see if there is one or many types of paramagnetic centers. On this purpose the irradiated samples were been heated directly in the resonance cavity 10 minutes every 10 degrees in the range of temperature between room temperature and $+200^\circ\text{C}$, recording the spectra. Some of the recorded spectra are given in Fig.5.

From the figure one observes that the most intense line of the spectrum decreases by heating and at about 73°C practically disappears. To note that the diminution of this line intensity was observed also when we preserve the irradiated samples for few days at room temperature. By measuring the spectral characteristics of this line we observed that these correspond with those of the centre A in the case of γ irradiation. It is to be mentioned also that the other two lines which remained from the spectrum after heating, appear

at the same fields as those noted with B and C respectively, in the EPR spectra of the samples γ irradiated. The intensity of these last lines practically does not vary up to 65°C, and then they begin to decrease. This behaviour is well put into evidence if we represent the variation of the intensities of the lines A, B and C versus the heating temperature (Fig.6).

The center B proved to be the most resistant to the heating. Thus one can observe it even after the sample heating at 190°C, while the others disappeared. In this conditions we could observe the correct form of the center B in the spectrum (see Fig.7) and we could determine the g-values :

$$g_{\parallel} = 2.0042 \pm 0.0005$$

$$g_{\perp} = 2.0148 \pm 0.0005$$

No hyperfine structure was observed.

The lines C, less intense than the others, are observable up to 130°C.

Samples of NaReO_4 powder were irradiated also with neutrons with a flux of 10^{12} n/cm².s. for 6 hours (ϕ integral = 2×10^{16} n/cm²). The samples were stored at room temperature after irradiation for 16 days before the EPR spectrum being recorded. This has a pattern near of those obtained in NaReO_4 samples irradiated with 3 MeV electrons after standing a similar time at room temperature. In this case also one observes the lines A, B and C. Concerning the lines C, it is apparent that with neutron irradiation these are more intense than in the γ and electron irradiation, which indicates the formation of a greater concentration of the corresponding paramagnetic center. This fact allowed us to determine the EPR spectral parameters for this center too. In view to minimize the overlapping from the central part of the spectrum, the neutron irradiated samples

were heated at 90°C for about 1 hour when the concentration of the other centers sensible decreased (Fig.8).

In these conditions one observes (excluding the small components which remained from the lines A and B) that the spectrum of the center C has a shape characteristic for a radical with an orthorombic g tensor ($g_1 \neq g_2 \neq g_3$) having the values :

$$g_1 = 2.0387 \pm 0.0007, \quad g_2 = 2.0135 \pm 0.0007, \quad g_3 = 1.9608 \pm 0.0007.$$

No hyperfine structure was observed.

$KReO_4$. Samples of $KReO_4$ polycrystalline powder were γ irradiated with the 16.000 Ci ^{60}Co source, in the same conditions as $NaReO_4$ samples. EPR spectra present a similar form with those of $NaReO_4$ γ irradiated samples (Fig.9).

The analysis of the obtained spectrum showed that A and C centers which were put into evidence in $NaReO_4$ are well observed also in this case, but is more difficult to distinguish the E signal because of their low intensity.

The g-values of A centres, determined from this spectrum were

$$g_{\parallel} = 2.0093 \pm 0.0005, \quad g_{\perp} = 2.0023 \pm 0.0005$$

The agreement between these values and those from EPR spectra of irradiated $NaReO_4$ proves that we have the same type of centres. But, it is to be mentioned that, in this case, their relative concentration is much smaller than in the $NaReO_4$ irradiation in the same conditions.

In the case of C centres, we obtained

$$g_1 = 2.004, \quad g_3 = 1.960$$

We could not determine the g_2 -value because of the overlapping in the central part of the spectrum of three lines coming from A, B and C centres. Even the two values which we could determine were measured with a smaller precision than in the other cases, due to the small signal intensity. However, a satisfactory agreement was obtained with the corresponding values of the center C in NaReO_4 .

The lines of the B center are observed only as shoulders, making difficult the EPR spectral parameters measurements.

Samples of polycrystalline KReO_4 were irradiated with 3 MeV electrons, at room temperature, obtaining EPR spectra with sufficient intensity. The shape of the spectrum was perfect similar with that of the spectra recorded in the irradiated NaReO_4 , then the same paramagnetic species are formed. After 24 hour at room temperature, these centres disappeared in KReO_4 , while in NaReO_4 they can be observed well enough.

We tried also to irradiate polycrystalline KReO_4 with neutrons, with integral fluxes of 10^{17} n/cm². EPR spectra recorded after 8 days from the end of irradiation evidenced some weak signals, for which was difficult to determine with accuracy the spectral parameters.

DISCUSSION

From the above results, it follows that by NaReO_4 and KReO_4 irradiation in identical conditions similar EPR spectra are recorded, indicating that in both samples the same paramagnetic centres are formed. The lower intensity of the spectra recorded in the KReO_4 irradiated samples shows a higher radio-

resistence of the KReO_4 than that of NaReO_4 .

In the EPR spectra of the samples irradiated γ , with electrons and with neutrons, the presence of three paramagnetic species noted A, B and C was observed. It seems that the nature of radiation used does not affect the nature of paramagnetic centers observed in both irradiated perrhenates, but affects the relative concentrations of the three centres.

Concerning the nature of the paramagnetic species, the irradiation of NaReO_4 and KReO_4 could lead to the formation of following radicals : ReO_4^{2-} , ReO_4^\cdot , ReO_3^{2-} , ReO_3^\cdot and ReO_2^\cdot .

ReO_4^{2-} is an electron adduct radical. According to Balhausen and Liehr /5/ scheme of the molecular orbitals for d^1 tetroxianions, the unpaired electron in this kind of radical is in an molecular orbital E which has contributions from the 5d atomic orbital of Re as well as from the 2p orbitals of the oxygen. Thus it would be expected that the EPR spectrum of this radical presents a hyperfine structure with six components - Re having two isotopes (^{185}Re - 37.07% and ^{187}Re - 62.93%) both of them with the nuclear spin $I = \frac{5}{2}$. Concerning the values of the g tensor, these would be all sensible smaller than the free spin value. This kind of tetroxianion radicals of the transition metals, formed by irradiation, was observed in few cases as for example WO_4^{3-} in CaWO_4 /6/ and MnO_4^{2-} in irradiated KMnO_4 /7/.

Inasmuch none of the three radical species observed by NaReO_4 and KReO_4 irradiation presents these characteristics, it seems reasonable to consider that, in these cases, by irradiation do not form ReO_4^{2-} radical stable in the range of temperature in which we worked.

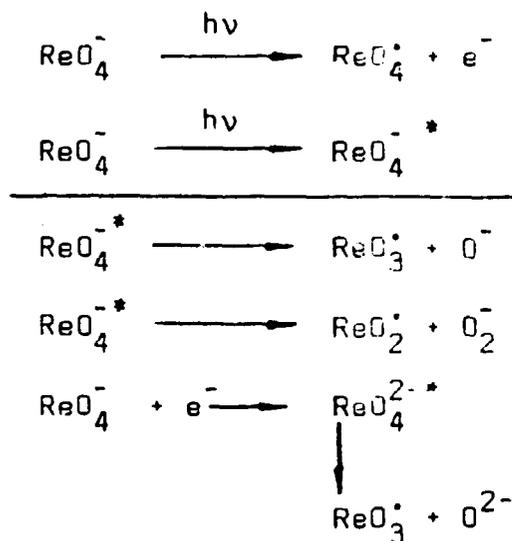
The radical ReO_4^\bullet is a hole center the ground state of which would be 2T_1 molecular orbital with contributions only from the atomic orbitals of the oxygen ligands. The unpaired electron is delocalized on the oxygen atoms and the hyperfine coupling to rhenium would be weak and could occur only by configuration interaction. The g-values should be something higher than the free-spin value, but close to this.

From the three paramagnetic centers observed, the A center (the major species in both perrhenates, in all irradiation conditions) do not present a hyperfine structure, has the values of g-tensor some higher than the free spin value and is less thermoresistant (as usual XO_4^\bullet type radicals) /8/, thus we considered that this would be an radical of ReO_4^\bullet type, formed by an electron lost.

The paramagnetic center noted B, formed in smaller concentration and more resistant by heating than A, has an axial symmetry (which is usually known for the radical of XO_3^\bullet type), the g values higher than the free spin value, and no hyperfine structure. On the basis of this characteristics, we assigned the B center to a radical of ReO_3^\bullet type.

Finally, the C center, formed in very low concentration, without hyperfine structure, having $g_1 \neq g_2 \neq g_3$, has the characteristics of the XO_2^\bullet type radicals /9/. For this, we postulate that the C species is ReO_2^\bullet .

On the basis of the assignment above mentioned of the paramagnetic centres observed by NaReO_4 and KReO_4 irradiation, the following radiolytical scheme (taking into account only the paramagnetic centers formation) can be proposed :



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FIGURE CAPTIONS

- Fig.1. EPR spectrum of polycrystalline NaReO_4 irradiated at 77 K, with an integral dose of 4.6 Mrad (rate dose 1.15 Mrad/h) and recorded at the same temperature.
- Fig.2. EPR spectrum of a NaReO_4 polycrystalline sample γ irradiated at 77 K and heated 10 minutes at :
- | | |
|-------------------------|------------------------|
| a) -145°C | e) -65°C |
| b) -125°C | f) -45°C |
| c) -105°C | g) -25°C |
| d) -85°C | h) room temperature. |
- Fig.3. Isochrone variation with the temperature of the A signal intensity for NaReO_4 irradiated at 77 K with an integral dose of 4.6 Mrad.
- Fig.4. EPR spectrum of polycrystalline NaReO_4 irradiated at room temperature with 3 MeV electrons, recorded at the same temperature (integral dose 22 Mrad).
- Fig.5. EPR spectra of a NaReO_4 sample irradiated at room temperature with 3 MeV electrons ($D_i = 22$ Mrad) and heated at different temperatures :
- | | |
|-----------------------|------------------------|
| a) room temperature | d) 103°C |
| b) 73°C | e) 113°C |
| c) 93°C | f) 133°C |

Fig.6. The isochrone variation with temperature of the lines intensities from the EPR spectrum of NaReO_4 irradiated with 3 MeV electrons ($D_i = 22$ Mrad).

Fig.7. EPR spectrum of a NaReO_4 sample irradiated with 3 MeV electrons ($D_i = 22$ Mrad) after heating for 1 hour at 190°C .

Fig.8. EPR spectrum of a NaReO_4 neutron irradiated sample ($\phi_{\text{int}} = 2 \times 10^{16}$ n/cm²) after heating for 1 hour at 90°C .

Fig.9. EPR spectrum of a KReO_4 sample γ irradiated at 77 K with an integral dose of 4.6 Mrad. recorded at the same temperature.

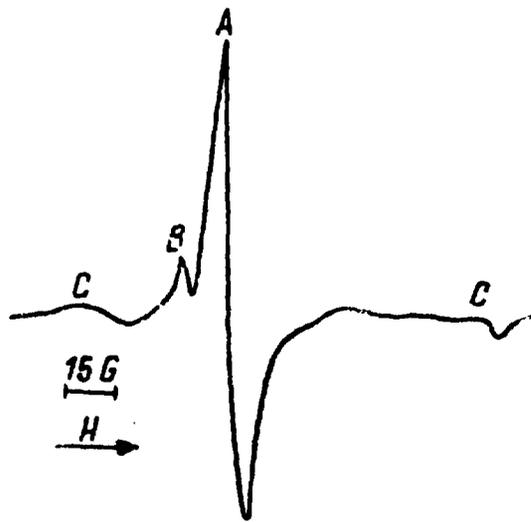


Fig. 1

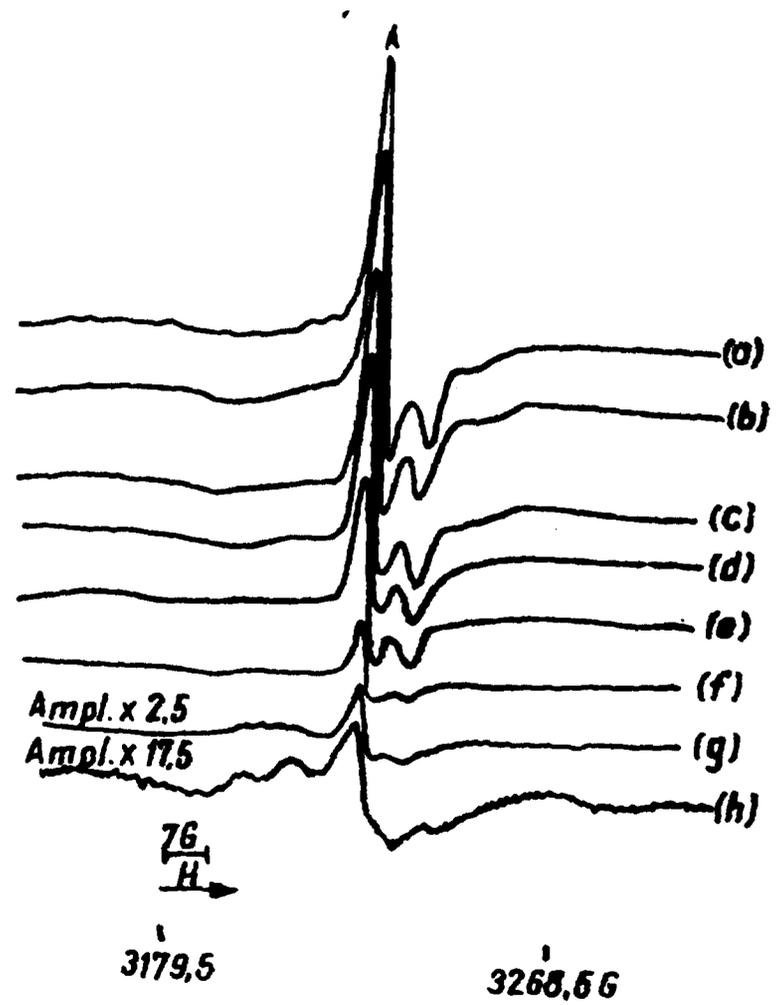


Fig. 2

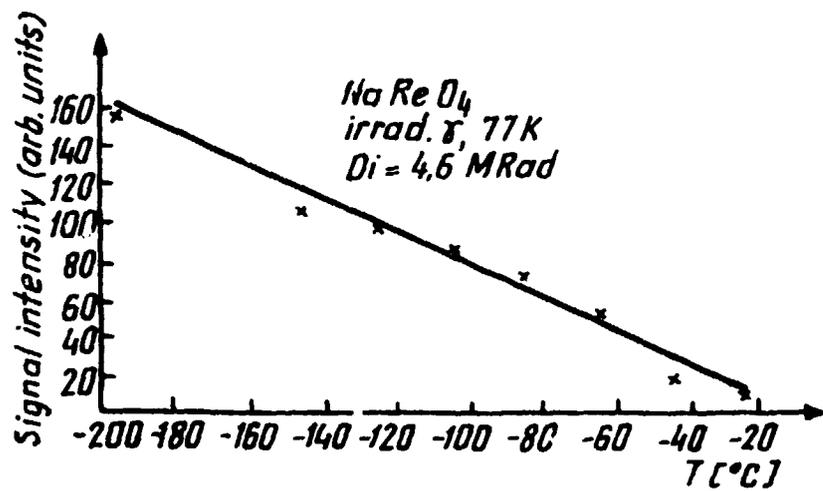


Fig. 3

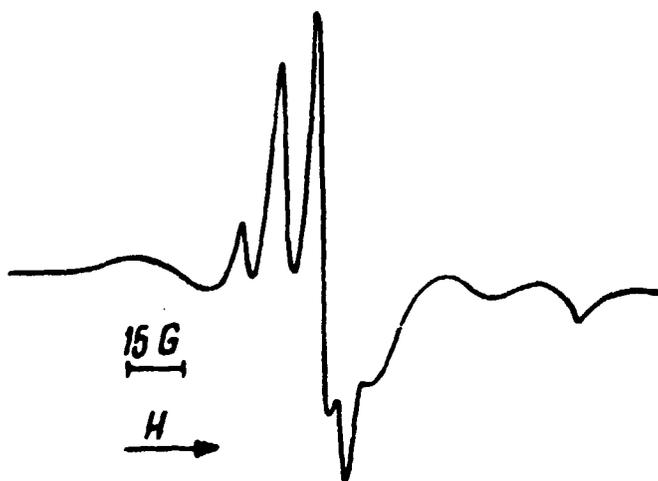


Fig. 4

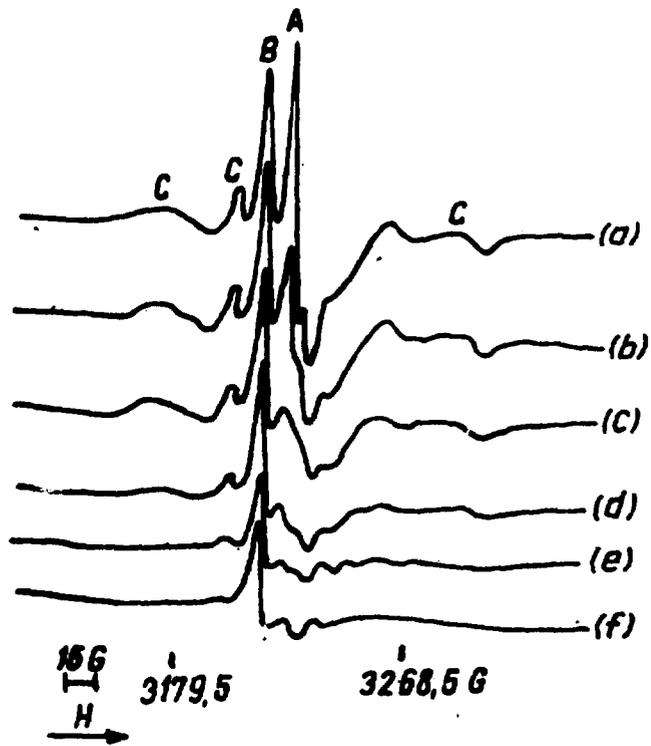


Fig. 5

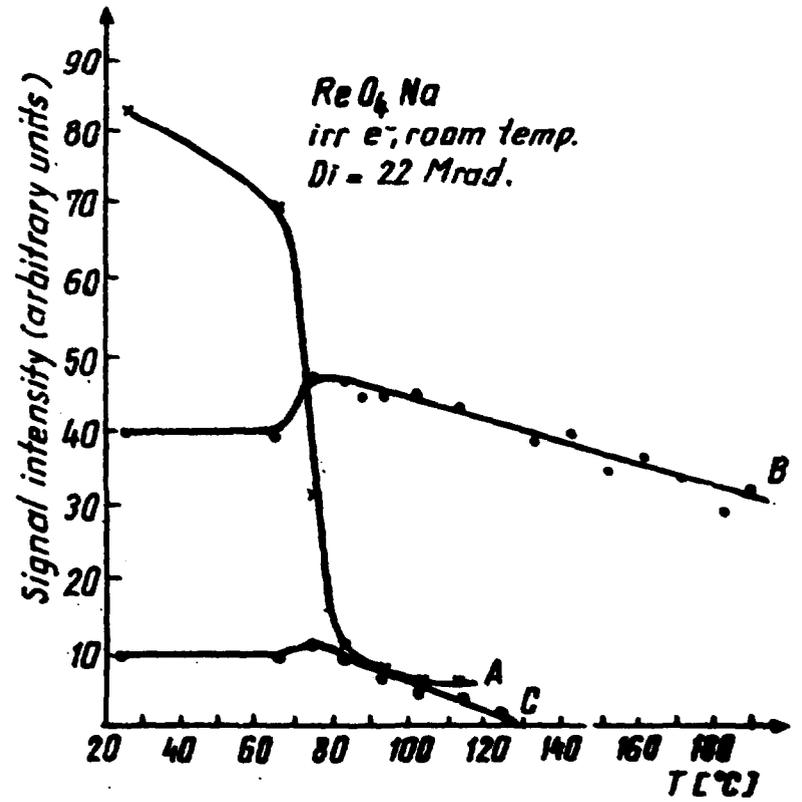


Fig. 6

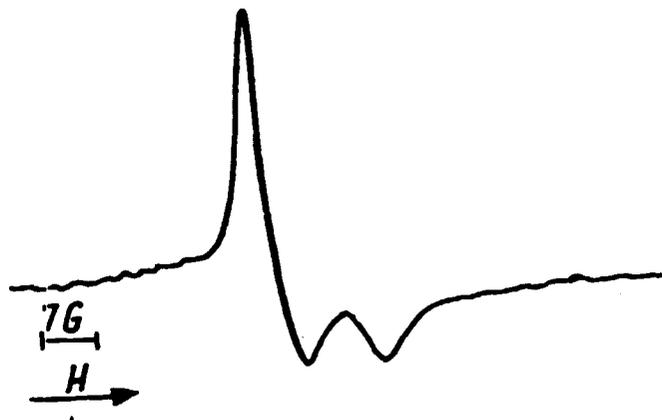


Fig. 7



Fig. 8

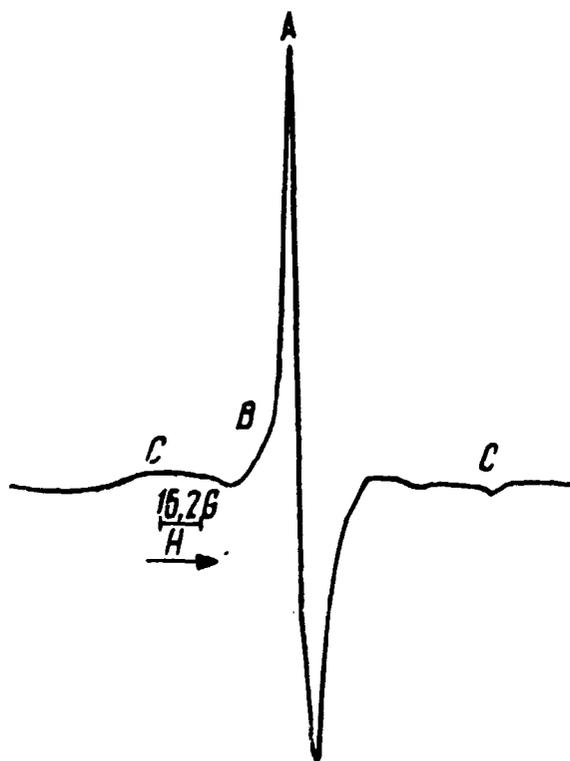


Fig. 9



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