

Gadolinium(III) cryptates investigated by multifrequency EPR

Andrzej Szczyzewski^{a,*}, Stefan Lis^b, Jerzy Krzystek^c, Krzysztof Staninski^b,
Andrzej Kłonkowski^d, Zdzisław Kruczyński^a, Marek Pietraszkiewicz^e

^a Faculty of Physics, A. Mickiewicz University, Umultowska 85, Poznań, Poland

^b Faculty of Chemistry, A. Mickiewicz University, Grunwaldzka 6, Poznań, Poland

^c National High Magnetic Field Laboratory, Florida State University, Dirac Dr., Tallahassee, FL 32310, USA

^d Institute of Chemistry, University of Gdańsk, Sobieskiego 18, Gdańsk, Poland

^e Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/48, Warszawa, Poland

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Abstract

EPR studies of Gd(III) with the hexa(diphenylphosphinoxide)-cyclotriphosphazene ligand, PNP, can provide information about local environment of the Gd(III) ion. Furthermore, analysis of the EPR spectra of the Gd(III) PNP complex, carried out at X- and W-band (9.4 and 94 GHz) frequencies, provided information on the phase transition near 5.4 K as well as information on the time durability of the Gd/PNP complexes in the SiO₂ xerogel matrix.

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1. Introduction

Recently, a great deal of attention has been paid to the chemical properties of the rare-earth elements because of their use in magnetic and optical devices as well as their utility as luminescence probes and as catalysts in organic syntheses. Electron paramagnetic resonance (EPR) spectroscopy of the Gd³⁺ ion, with a 4f⁷ electronic configuration (⁸S_{7/2}), can be observed at room temperature. EPR is a very powerful method of studying the magnetic properties and crystal-field symmetry of the lanthanide(III) complexes. Since spin-lattice relaxation times are shortened due to the very strong spin-orbit coupling in Ln(III) ions, the EPR spectra can be best observed at very low temperatures. Furthermore, the structure and stability of rare-earth complexes in solution are attracting interest because the gadolinium(III) complexes have been found to be useful as contrast agents for magnetic resonance imaging (MRI) [1]. It is very useful to study the properties of the 4f-electrons by using coordination complexes because the local environment of the Ln(III) ions can be controlled through chemical modification of the ligands.

The spin Hamiltonian of the Gd(III) ion is known to be [2]:

$$H = g_0\beta BS + D \left[S_Z^2 - \frac{1}{3}S(S+1) + E(S_X^2 - S_Y^2) \right] \quad (1)$$

where g is the g -value of the S-state, D and E are the zero-field splitting parameters. Usually Eq. (1) can be treated considering perturbation theory in two cases:

1. Strong Zeeman interactions, when $g\beta B \gg D, E$. In this case the EPR spectrum consists of a single very broad line of $g=2.0$, which indicates strong Zeeman interactions and a weak crystal field. contribute to chemical bonds and formation of complexes.
2. Strong crystalline field, $D, E \gg g\beta B$.

There is the eight-fold spin degeneracy of the Gd(III) free ion with $S=7/2$. The strong crystal field splits the free-ion level into four doubly degenerate energy levels. The magnetic field removes such remaining degeneracy. As a result the transitions of unpaired electrons between these eight split levels with $g \gg 2.0$ and $g < 2.0$ are observed. The presence of these lines indicates the case of the strong crystal field.

If the Zeeman microwave frequency is of the same order as the crystal-field strength, the zero-field resonance can be observed. So, one can ascertain that the EPR spectrum of Gd(III)

* Corresponding author. Fax: +48 61 825 77 58.

E-mail address: aszy@amu.edu.pl (A. Szczyzewski).

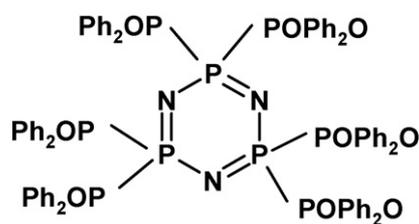


Fig. 1. Structure of PNP molecule.

ion depends on the relation between crystal field strength and Zeeman interactions.

In the series of our previous studies we have investigated an influence of the local environment of the Gd(III) ion on EPR spectra of several groups of Gd(III) complexes such as: β -diketonates and aminopolycarboxylates, heteropolyanions, as well as sandwiched and encapsulated polyoxometalates [3–7].

The aim of this work is to study complexation properties of the materials consisting of Gd(III) complex with the PNP ligand, entrapped in silica and silica modified (PDMS and Glymo) matrices, prepared by the sol–gel procedure. This ligand forms with the Ln(III) ions (Eu and Tb) complexes of promising luminescence properties. The Eu(III) and Tb(III) ions present in the investigated materials are not able to give EPR spectra at room temperature, however, they can be substituted by Gd(III) showing EPR, at this temperature.

For low-symmetry systems, particularly in frozen solution samples, the standard EPR suffers from low spectral resolution because of strong inhomogeneous line broadening. Such problems arise, for instance, because several paramagnetic species or different magnetic sites of rather similar g -values are present. The small g -tensor anisotropy of the paramagnetic system does not allow canonical orientations of the powder EPR spectrum to be observed. For improving the spectral resolution we use the high-field EPR operating at W-band (94 GHz).

2. Experimental

2.1. Synthesis of compounds

Synthesis of hexa(diphenylphosphinoxy)-cyclotriphosphazene, PNP (Fig. 1).

Hexachlorocyclotriphosphazene (10 mmol) was dissolved in 50 mL of THF freshly distilled over lithium aluminum hydride under Ar, and treated with 60 mmol of potassium diphenylphosphide (solution in THF). The reaction is exothermic. The clear solution was gently heated for 2 h at 50 °C, cooled and treated with 60 mmol of 30% hydrogen peroxide with efficient cooling. The solvent was evaporated and the residue was crystallised from acetone to yield white product with 95% yield. The Gd(III) complex was prepared by treatment of methanolic solution of the ligand with Gd(CF₃SO₃)₃ (1:1 molar ratio) at reflux, and filtering.

The Gd(III) complex was immobilized into silicate, methylated silicate of PDMS (polydimethylsiloxane) and organically modified with Glymo (3-glycidoxypropyl-trimethoxysilane) silicate xerogels were synthesized according to the preparation procedure described previously [8].

2.2. Methods

EPR spectra were recorded as the first derivatives of absorption using a Bruker ESP 300E X-band (Poznan) and Bruker Elecsys E680X spectrometers (Tallahassee) at the X- and W-bands frequencies (9.4 and 94 GHz). These spectra

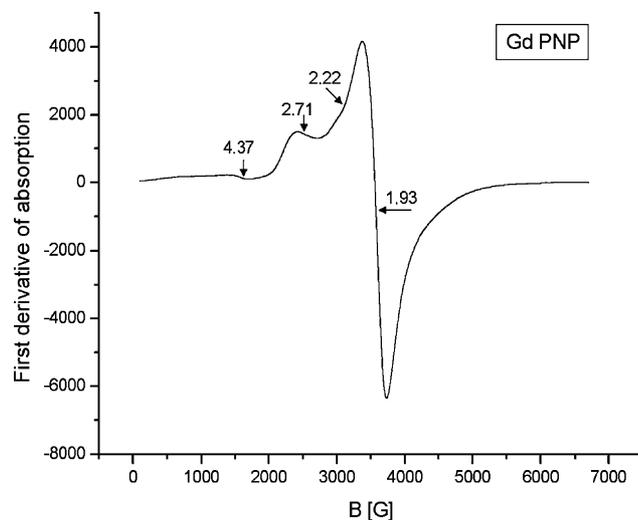


Fig. 2. X-band (9.4 GHz) EPR spectrum of Gd PNP registered in room temperature.

were recorded at room temperature and some of them in temperatures between 5 and 200 K.

The W-band (94 GHz) EPR increases the Zeeman splitting as compared to conventional X-band EPR experiments by approximately one order of magnitude and should thereby permit overcoming some difficulties in interpretation of complicated EPR spectra. The increased Zeeman splitting also helps to separate given contributions to the spectrum.

All samples in this work have been studied in the form of polycrystalline powders.

3. Results and discussion

The EPR spectrum of Gd/PNP complex, **I**, recorded at X-band EPR exhibits the following lines with effective g -values of 1.93, 2.22, 2.71 and 4.37 (Fig. 2). This complex immobilized in the SiO₂ xerogel, **II**, gives the EPR spectrum, which lines characterize the following effective g -values: 4.16, 2.67, 2.59, 2.24, 1.93, 1.59 (Fig. 3). The significant difference between these spectra results from the mutual intensity ratio of the central lines

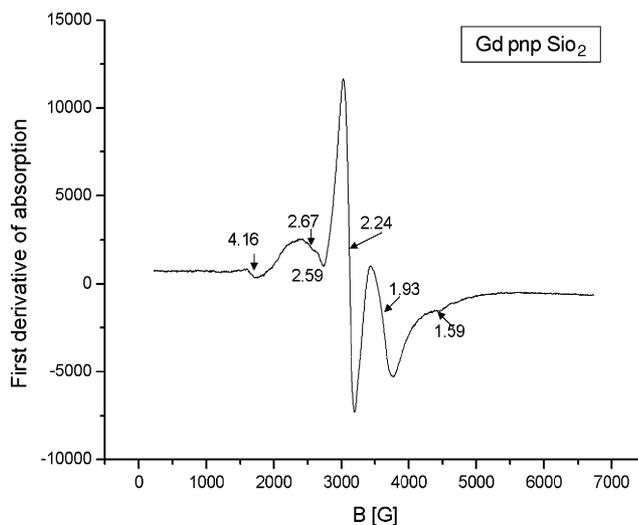


Fig. 3. X-band (9.4 GHz) EPR spectrum of Gd PNP in the SiO₂ xerogel matrix registered in room temperature.

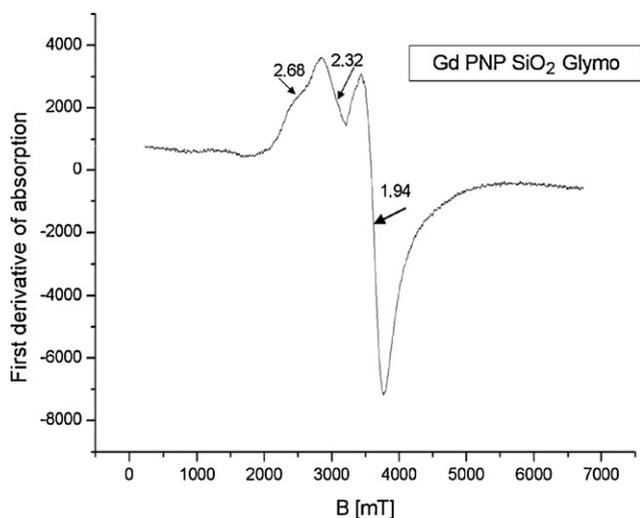


Fig. 4. X-band (9.4 GHz) EPR spectrum of Gd PNP in the SiO₂:Glymo xerogel matrix registered in room temperature.

with effective g -values 2.24 and 1.93, respectively. In the spectrum of **I** the line of 1.93 is much more intense than in the case of **II**; however, in **II** the line of 2.24 is dominating one. The complex Gd/PNP entrapped into the SiO₂ Glymo modified matrix, **III** (Fig. 4) having in its structure additionally organic molecule, shows an EPR spectrum similar to **I** with characteristic lines of effective g -values 1.94, 2.32, 2.68. It can be a result of stabilizing of the Gd/PNP complex caused by Glymo increasing stability in this matrix. The same spectral features were observed in the case of the SiO₂:PDMS matrix (Fig. 5).

The intensity of the two central lines in the X-band EPR spectrum is time dependent. The EPR spectra of **II** measured directly after the synthesis (Fig. 2) and about 1 year later (Fig. 6) differ each other considering their line intensities of 1.93 and ~ 2.2 . Initially the line of ~ 2.24 was more intensive, while after 1 year the line of 1.93 was dominating.

The measurements of EPR spectra were also carried out in the W-band (94 GHz) in the temperature range 293–5.4 K for the

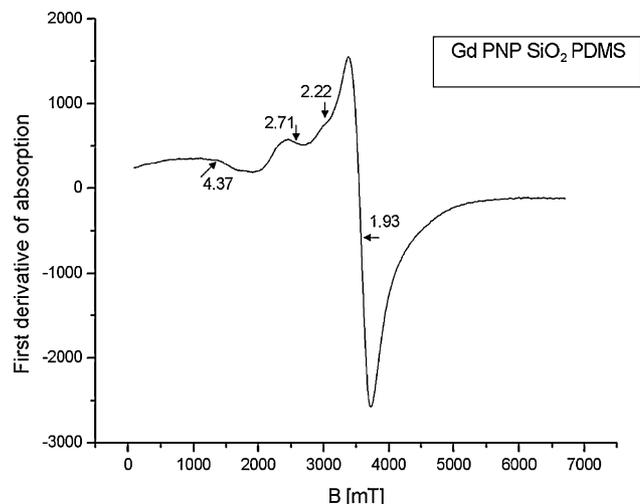


Fig. 5. X-band (9.4 GHz) EPR spectrum of Gd PNP in the SiO₂:PDMS xerogel matrix registered in room temperature.

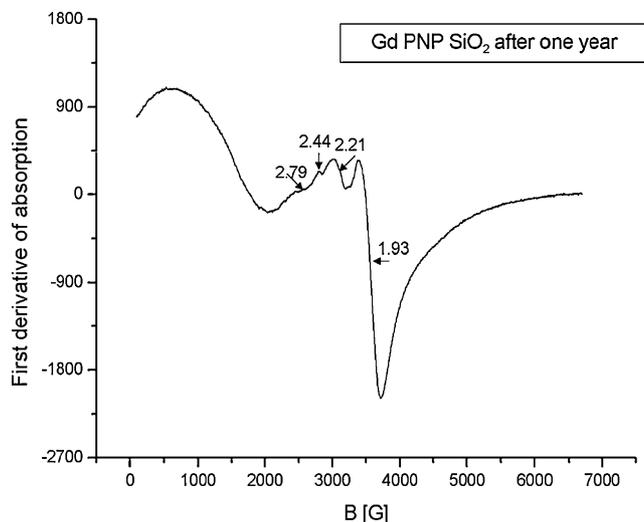


Fig. 6. X-band (9.4 GHz) EPR spectrum of Gd PNP in the SiO₂ xerogel matrix registered in room temperature 1 year later.

Gd/PNP in the SiO₂ matrix (Fig. 7). At the temperature range studied the characteristic line of $g_{\text{eff}} \approx 1.99$ is observed. In the room temperature the spectrum exhibit additionally shoulders at 2.033 and 1.935, respectively. At temperature 40 K a line of $g_{\text{eff}} \approx 1.93$ appears, which intensity rapidly increases at 5.4 K. The most evident changes were observed in the temperature range between 10 and 5 K (Figs. 7–9), when the line width (peak to peak) of $g_{\text{eff}} 1.99$ step-wise increases from ~ 260 to ~ 530 G. At the same temperature (5.4 K) the intensity of the 1.93 line significantly increases, whereas the line width (peak-to-peak) decreases from 730 to 640 G in the temperature range of 10–5.4 K.

EPR spectral features of Gd(III) ion depend as has been mentioned before on the relative magnitude of microwave frequency and crystal field strength. When the microwave frequency is small compared with crystal field strength, EPR lines of Gd(III) appear in the range of $g > 2.0$. If there are prominent features in the vicinity of $g = 6.0$, 2.8 and 2.0 on the spectrum, then

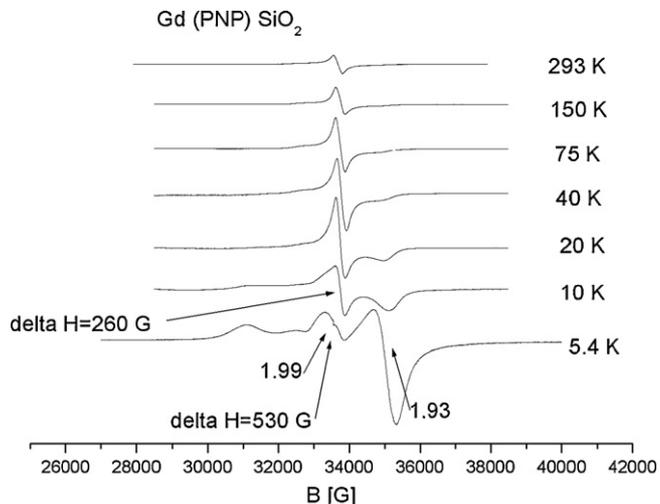


Fig. 7. Temperature dependence of W-band (94 GHz) EPR spectra of Gd PNP SiO₂ registered in region 293–5.4 K.

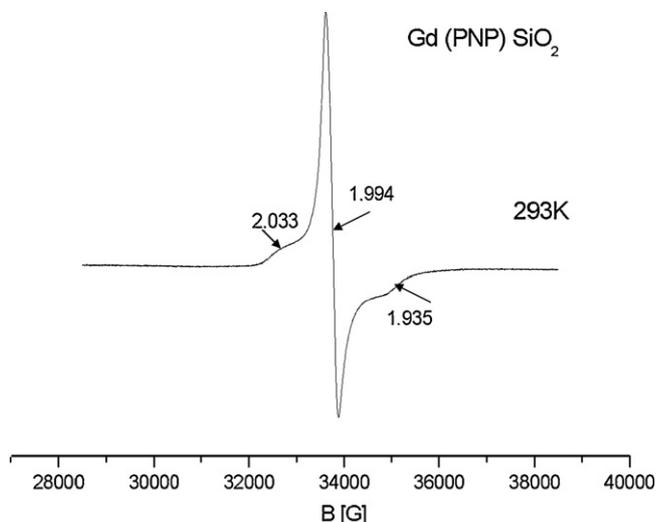


Fig. 8. W-band (94 GHz) EPR spectrum of Gd PNP in SiO₂ xerogel matrix registred in 293 K.

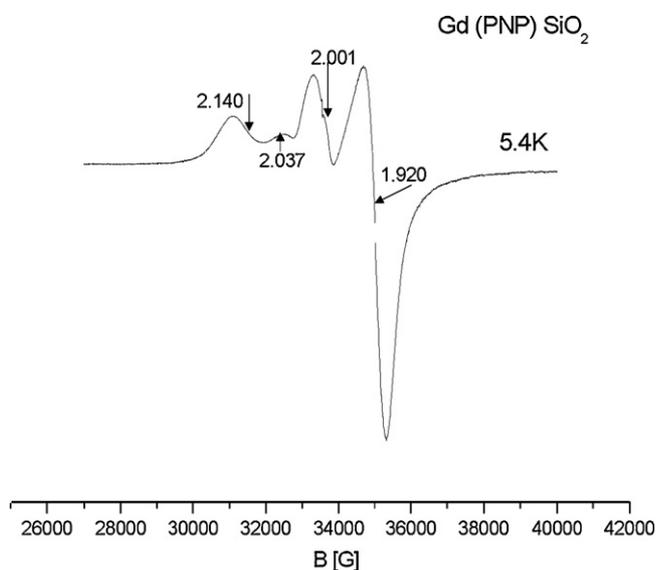


Fig. 9. W-band (94 GHz) EPR spectrum of Gd PNP in SiO₂ xerogel matrix registred in 5.4 K.

the spectrum is called “U” spectrum as described in [9–11]. When the microwave frequency is of the same order of the crystal field strength, the zero-field resonance can be observed. If the microwave frequency is larger than that of the crystal field strength, the EPR transition will be concentrated in the vicinity of $g \approx 2.0$.

As is known from the work [12] the line width of the EPR spectra of Gd ion is broadened with the decrease of temperature. It is due to the spin–spin interaction between the Gd–Gd ions. An increase of the spin–spin interaction with the decrease of temperature causes the broadening of lines.

In the case of the W-band we observed that the temperature dependence the EPR spectra of Gd/PNP in the xerogel matrix, in

contrary to [12] is different. The line width (peak to peak) of $g_{\text{eff}} 1.99$ for Gd(III) ion is constant and has a value of ~ 260 G in the temperature range of 293–10 K, and only in the temperature range 10–5.4 K rapidly doubly increases to 530 G. This fact and the change of the intensity ratio of 1.99 and 1.93 lines seems to support the existence of the temperature phase transition as a consequence of structural changes in the system studied.

This is the first information about the phase transition observed by EPR studies concerning Gd(III) complexes immobilized in xerogel matrices.

The Gd(III) ion in the systems studied in the low temperature phase (5.4 K), according to the above suggestion fills a stronger crystal field than in the high temperature phase. A similar character of a behavior of the two central lines of $g_{\text{eff}} = 2.24$ and 1.93 in the X-band EPR spectrum of the GDPNP complex in the SiO₂ matrix (the intensity ratio changes in time) seems to demonstrate that the phase transition also takes place in the materials as a function of time. It should be also emphasized that the modification of the xerogels (by PDMS and Glymo) influences the complex stabilization. Studies on these Gd(III) systems are underway.

4. Conclusions

Analysis of the EPR spectra of the Gd(III)/hexa(diphenylphosphinoxide)-cyclotriphosfazene complex, carried out at X- and W-band (9.4 and 94 GHz) frequencies, provided information on the phase transition near 5.4 K and information on the time durability of the Gd/PNP complexes immobilized in the SiO₂ xerogel matrix.

The existence of the temperature phase transition as a consequence of structural changes in the system studied was observed for the first time by EPR studies concerning Gd(III) complexes.

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