

ELECTRON PARAMAGNETIC RESONANCE IN GLASSES CONTAINING RARE-EARTH ELEMENTS

PHYSICS

1967

SovietRxiv

View the original and related papers at <https://sovietrxiv.org/items/ru-196701.41870>

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

Abstract

Full Text

UDC 538.222

PHYSICS

T. S. AL' TSHULER

**ELECTRON PARAMAGNETIC RESONANCE
IN GLASSES CONTAINING RARE-EARTH
ELEMENTS**

(Presented by Academician E. K. Zavoisky, 13 VII 1966)

Glasses containing rare-earth elements have not been studied by the EPR method, with the exception of the case of two ions, Gd^{3+} and Eu^{2+} , which are in the S -state ⁽¹⁾. The absence of such studies is apparently connected with the large anisotropy of the g -factor and with short relaxation times.

In the present article the results are reported of a study of EPR spectra in low-temperature glasses containing Nd^{3+} and Cl^{3+} ions. Measurements were carried out at frequencies $\nu = 300$ -400 MHz and $\nu = 9500$ MHz at a temperature of 4.2° K. The main results of the study are given in Table 1.

Table 1

| Complex | Solvent | δH | g_{eff} | $g_{ }$ | g_{\perp} |
|--------------------------|--------------------------|--------------------|--------------------|---------------------|---------------------|
| | | $\nu = 300$ MHz | $\nu = 300$ MHz | $\nu = 9500$ MHz | $\nu = 9500$ MHz |
| $NdCl_3 \cdot 6H_2O$ | Ethanol | 30 | 2.5 ± 0.1 | 2.29 ± 0.01 | 3.04 ± 0.01 |
| $NdCl_3 \cdot 6H_2O$ | Methanol | 43 | 2.3 ± 0.1 | Not studied | Not studied |
| $NdCl_3 \cdot 6H_2O$ | Hydrochloric acid 38% | 42 | 2.1 ± 0.1 | 2.23 ± 0.01 | 3.13 ± 0.01 |
| $NdCl_3 \cdot 6H_2O$ | Hydrochloric acid 19% | 36 | 2.3 ± 0.1 | 2.25 ± 0.01 | 3.05 ± 0.01 |
| $NdCl_3 \cdot 6H_2O$ | Glycerin | 50 | 2.4 ± 0.1 | 1.94 ± 0.01 | 3.04 ± 0.01 |
| $NdCl_3$ | Ethanol | 32 | 2.4 ± 0.1 | 2.15 ± 0.01 | 3.15 ± 0.01 |
| $NdCl_3$ | Methanol | 32 | 2.4 ± 0.1 | Not studied | Not studied |
| $Nd(NO_3)_3 \cdot 6H_2O$ | Ethanol | 60 | 2.4 ± 0.1 | | |
| $Nd(NO_3)_3 \cdot 6H_2O$ | Hydrochloric acid | 83 | 2.2 ± 0.1 | | |

| Complex | Solvent | δH | g_{eff} | g_{\parallel} | g_{\perp} |
|--|---|------------|------------------|-----------------|-------------|
| Nd(CNS) ₃ | 6H ₂ O phos- phate | 59 | 2.4 ± 0.1 | | |
| Nd(CNS) ₃ | 6H ₂ O phos- phate | 53 | 2.1 ± 0.1 | | |
| Nd(C ₂ H ₃ O ₂) ₃ | Glycolic acid | 40 | 2.3 ± 0.1 | 2.03 ± 0.01 | 3.08 ± 0.01 |
| CeCl ₃ | 6H ₂ O Ethanol | 123 | 2.2 ± 0.1 | | |
| CeCl ₃ | 6H ₂ O Hydrochloric acid | 140 | 1.8 ± 0.1 | | |
| Ce(NO ₃) ₃ | 6H ₂ O Ethanol | 78 | 2 ± 0.1 | | |
| Ce(NO ₃) ₃ | 6H ₂ O acid | 160 | 1.6 ± 0.1 | | |
| Ce(CNS) ₃ | 7H ₂ O phos- phate | 36 | 2.1 ± 0.1 | 2 + 0.001 | 2.48 ± 0.01 |
| Ce(CNS) ₃ | 7H ₂ O phos- phate with hy- drochlo- ric acid | 100 | 2 ± 0.1 | | |

All the glasses we studied that contain Nd³⁺ and Ce³⁺ give an intense EPR signal at low frequencies. In neodymium chlorides and in cerium rhodanides, almost symmetric and comparatively narrow (Fig. 1a, b) EPR lines with $\delta H = 30$ -50 Oe are observed at a concentration of the paramagnetic ion of 0.12 *M*. The remaining cerium and neodymium compounds give asymmetric lines with a width of the order of $\delta H = 60$ -160 Oe. In those cases in which the line width at low frequencies did not exceed 50 Oe, it was possible to obtain an EPR signal also at high frequencies. At $\nu = 9500$ MHz, very broad, asymmetric (Fig. 1b, c) lines were observed, from whose appearance it is pos-

to determine the values of g_{\parallel} and g_{\perp} . In the remaining glasses listed in Table 1, the EPR line was not observed at high frequencies; this is undoubtedly associated with the strong anisotropy of the g -factor.

Investigation of the line shape makes it possible to conclude that the total width

$$\delta H = \delta H_{\text{anis}} + \delta H_{\text{el}} + \delta H_{\text{magn}}.$$

The quantity

Fig. 1. EPR spectra in low-temperature glasses at 4.2 K. *a* $-\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ in ethanol, $\nu = 300$ MHz; *b* $-\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ in ethanol, $\nu = 9500$ MHz; *c* $-\text{Ce}(\text{CNS})_3 \cdot 7\text{H}_2\text{O}$ in triethyl phosphate, $\nu = 300$ MHz; *d* $-\text{Ce}(\text{CNS})_3 \cdot 7\text{H}_2\text{O}$ in triethyl phosphate, $\nu = 9500$ MHz; $g = 2.0004$ is indicated by the vertical arrow

Figure 1: Fig. 1. EPR spectra in low-temperature glasses at 4.2 K. *a* $-\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ in ethanol, $\nu = 300$ MHz; *b* $-\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ in ethanol, $\nu = 9500$ MHz; *c* $-\text{Ce}(\text{CNS})_3 \cdot 7\text{H}_2\text{O}$ in triethyl phosphate, $\nu = 300$ MHz; *d* $-\text{Ce}(\text{CNS})_3 \cdot 7\text{H}_2\text{O}$ in triethyl phosphate, $\nu = 9500$ MHz; $g = 2.0004$ is indicated by the vertical arrow

$$\delta H_{\text{anis}} = \frac{h\nu}{\beta} \left(\frac{1}{g_{\perp}} - \frac{1}{g_{\parallel}} \right)$$

is determined by the anisotropy of the g -factor and at high frequency gives the main contribution to the total width. Fluctuations of the local electric field, produced by the second and subsequent coordination spheres, cause a spread of g -factors and determine $\delta H_{\text{el}} = H \delta g$. At low frequency, increasing the concentration of rare-earth ions from 0.12 to 1 M causes a broadening of the lines δH_{magn} , which amounts on average to 30% of the entire width for Nd salts and approximately 10% for Ce salts. A rough estimate shows that δH_{magn} is due to dipole-dipole interactions between rare-earth ions. This is also confirmed by the experimentally observed symmetrization of EPR lines upon increasing the concentration of paramagnetic ions.

Fig. 1. EPR spectra in low-temperature glasses at 4.2° K.

a $-\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ in ethanol, $\nu = 300$ MHz;
b $-\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ in ethanol, $\nu = 9500$ MHz;
c $-\text{Ce}(\text{CNS})_3 \cdot 7\text{H}_2\text{O}$ in triethyl phosphate, $\nu = 300$ MHz;
d $-\text{Ce}(\text{CNS})_3 \cdot 7\text{H}_2\text{O}$ in triethyl phosphate, $\nu = 9500$ MHz;
 $g = 2.0004$ is indicated by the vertical arrow.

From the shape of the lines measured at low and high frequencies, it may be concluded that the rare-earth ion in all the compounds we studied is located inside an axially distorted octahedron. From optical ⁽²⁾ and X-ray structural ⁽³⁾ data it is known that halides of rare-earth ions in aqueous and alcoholic solutions form, respectively, a rhombically or triclinically distorted octahedron formed by six solvent molecules. But, apparently, these rhombic and triclinic distortions in our compounds are small compared with the axial ones and therefore do not affect the EPR spectrum. The observed change in the g -factors on going from one investigated salt to another is associated with a change in the degree of octahedral distortion. Study by the EPR method of alcoholic solutions of hydrated and anhydrous Nd chloride fully confirmed the optical and X-ray structural data ⁽²⁻⁴⁾ on the solvation of the rare-earth ion and on the

symmetry of the local electric fields. Neodymium chloride was dehydrated with thionyl chloride according to the procedure described in (5).

As is seen from Table 1, in alcoholic solutions of anhydrous NdCl_3 and $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ a rather strong difference is observed in g_{eff} and $g_{\parallel} - g_{\perp}$. These data allow one to conclude that in the first case alcohol solvation occurs, and in the second, hydration of the rare-earth ion. The decrease in anisotropy of the g -factor in hydrates indicates a higher symmetry of the field formed by water molecules than by alcohol solvates. When a small amount of water is added to an alcoholic solution of anhydrous NdCl_3 , the EPR line narrows slightly, which indicates the existence in solution of purely alcohol or purely hydrated solvates, since the formation of mixed solvation shells would lead to

to a lowering of the symmetry of the complex and to broadening of the EPR lines. In absolute methanol, NdCl_3 has exactly the same values of the g -factor, line width, and line shape as in ethanol solutions, which indicates complete identity of the symmetries of the local electric field. However, in the study of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ in absolute methanol (or of anhydrous NdCl_3 in an aqueous-methanol solution), a slight decrease in the g -factor and a rather considerable, by 20-30%, broadening of the EPR line are observed in comparison with the corresponding ethanol solutions. Taking into account that the solvation energy of methyl alcohol is practically equal to the hydration energy (6), one may suppose that mixed aqueous-alcohol solvates are formed in the aqueous-methanol solution. The observed lowering of the symmetry can be explained by the substantial difference between the dipole moments of water and alcohol (2).

Other explanations seem to us unlikely. In particular, since the second and subsequent coordination spheres cannot substantially change the g -factor and the line width, it is difficult to suppose that here, as in the case of aqueous-ethanol solutions, the rare-earth ion is surrounded by a purely hydrate shell. In view of the fact that the values of the g -factors and line widths lie outside the limits of the parameter values obtained for the Nd^{3+} ion in the case of a hydrate (aqueous-ethanol solution) and in the case of a solvate sphere, it may be concluded that the formation in solution of pure hydrates and pure alcohol solvates is also unlikely.

The small difference in the values of g_{eff} , $g_{\parallel} - g_{\perp}$, and in δH , observed in 38 and in 19% hydrochloric acid for the Nd^{3+} ion, is apparently explained by the fact that, with increasing water content in the solution, the hydration of the rare-earth ions also increases.

In the study of rhodanide complexes of Nd^{3+} extracted from aqueous solutions by tributyl phosphate (TBP) and triethyl phosphate (TEP), a substantial difference was observed in the g -factors and in δH . It is known that the solubility of TEP in water is much higher than that of TBP, and, apparently, it may be assumed that in TEP extracts, in addition to rhodanide-TEP solvates, less symmetric aqueous-rhodanide solvates also exist.

Observation of Ce rhodanide salts extracted by TEP from aqueous solutions showed that, when concentrated hydrochloric acid is added to the solution, the color of the complex changes and the width of the EPR lines increases by a factor of 2.5. From the studies of Yoshida ⁽⁷⁾ it is known that at high acidity the extraction of acid into the organic phase increases, and part of the rhodanide ions is bound according to the equation $H^+ + CNS^- + TBP \rightleftharpoons HCNSTBP$. This leads to deterioration of the stability of the complex and to an increase in the spread of local electric fields, which, in turn, leads to broadening of the EPR lines.

As can be seen from Table 1, the values of the g -factors of rare-earth salts in the glassy state differ strongly from the g -factors of identical salts measured on crystalline samples ⁽⁸⁾. This indicates a substantial difference between the local electric fields in crystals and in glasses. Thus, for example, crystals of $NdCl_3 \cdot 6H_2O$ and $Nd(NO_3)_3 \cdot 6H_2O$ have monoclinic symmetry, whereas in glasses, as indicated above, the Nd^{3+} ion is in fields of higher symmetry.

From observations at low frequencies it turned out that the lines are readily saturated. These experiments made it possible to estimate roughly the spin-lattice relaxation times. The estimate showed that T_1 in concentrated samples is equal to $1-2 \cdot 10^{-5}$, i.e., of the same order as in crystals ⁽⁹⁾. At the same time, in our glasses a dependence of the relaxation time on the concentration of paramagnetic ions was observed. Thus, upon dilution to 0.12 M , the times lengthen by approximately a factor of 2 for Nd salts and by a factor of 1.5 for Ce salts.

We also observed an EPR signal in alcoholic solutions of $Dy(SO_4)_3 \cdot 6H_2O$, $Yb(SO_4)_3 \cdot 6H_2O$, and $ErCl_3 \cdot 6H_2O$. Attempts to find an EPR signal in low-temperature glasses containing Sm^{3+} ions were unsuccessful. The absence of the signal is probably explained by the extremely small values of the g -factors ⁽⁸⁾ and by the resulting low signal intensity.

In conclusion, the author expresses deep gratitude to B. M. Kozyrev and N. S. Garif'yanov for supervising the work.

Kazan Physicotechnical Institute
Academy of Sciences of the USSR

Received
9 VII 1966

References

1. N. S. Garif'yanov, R. Kh. Timerov, N. F. Usacheva, FTT, 4, 3344 (1962).
2. I. I. Antipova-Karataeva, Yu. I. Kushenko, ZhKh, 9, 615 (1964).
3. G. W. Brady, J. Chem. Phys., 33, 1079 (1960).

4. V. Rotshtein, DAN, 71, 335 (1950).
5. C. Freeman, J. Inorg. and Nucl. Chem., 7, 286 (1958).
6. Z. I. Grigorovich, ZhNKh, 8, 986 (1963).
7. H. Yoshida, J. Inorg. Nucl. Chem., 24, 1257 (1962).
8. S. A. Al' tshuler, B. M. Kozyrev, *Electron Paramagnetic Resonance*, Moscow, 1961, pp. 132-134.
9. K. Jeffries, *Dynamic Orientation of Nuclei*, Moscow, 1965, p. 78.

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.