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EPR LINE SHAPE OF RARE-EARTH IONS IN DISORDERED SYSTEMS

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A calculation is presented of the EPR line shape in disordered systems with S = 1/2 and an arbitrary ratio $g_{\parallel}/g_{\perp}$. The calculations were performed under the assumption that the width of paramagnetic complexes with similar orientation in the magnetic field is determined by the scatter of the g factors. The calculated curves were used to analyze the EPR spectra of low-temperature glasses containing the rare-earth ions Ce^{3+}, Nd^{3+}, Dy^{3+}, and Yb^{3+}. The reason why $g_{\perp} > g_{\parallel}$ always in all the hitherto investigated glasses containing rare-earth ions is explained on the basis of certain assumptions concerning the symmetry of the crystal field.

1. INTRODUCTION

We know at present of a large number of ferromagnetic centers, the g-tensor components of which differ greatly from each other. When such centers are introduced into disordered systems (glasses, polycrystalline samples, etc), they produce very broad lines, as a result of which the direct determination of the g factors from the spectrum is impossible. We have encountered a similar situation in the investigation, by the EPR method, of low-temperature glasses containing rare-earth ions[1]. To be able to extract some information from the experimental data, we could use the line-shape theory for randomly oriented paramagnetic centers, proposed in a large number of papers[2-9]. However, only the paper of Ibers and Swalen[9] is free of the limitation that the anisotropy of the g-factor be small, i.e., $|g_{\parallel} - g_{\perp}| \ll g_{\parallel}$. Unfortunately, we were likewise unable to make use of the results of that paper, since these results were not in satisfactory agreement with experiment (see Fig. 3a below). The reason is apparently as follows. Let us denote by $\delta\nu$ the half-width of the individual resonance line (i.e., the line belonging to equally oriented paramagnetic complexes) in frequency units. It follows from the resonance conditions that the half-width in field units is equal to

$$\delta H = \gamma H, \tag{1}$$

where $\gamma = \delta\nu/\nu$. In[9], as well as in all the papers listed above, it is assumed that $\gamma \sim 1/H$, i.e., δH does not change with the field H. Yet frequently the broadening mechanisms lead to a dependence of δH on the magnetic field H. Let us consider one such case, when the only cause of the broadening of the "individual" resonance line is the scatter in the values of the g-factors. In polycrystalline samples, such a scatter arises, for example, as the result of crystal-lattice defects, while in glasses and in solutions it arises as the result of the difference between the second and subsequent coordination spheres of the paramagnetic complexes. If we denote by Δg the average positive fluctuation of the g-factor, then it follows from the resonance conditions that the average positive fluctuation of the magnitude of the resonance field is $\Delta H = (\Delta g/g)H$. The connection between Δg and the fluctuations of the electric field acting on the paramagnetic ion in condensed media is so complicated, that it can hardly be calculated. We have therefore made the natural assumption that $\Delta g = \text{const} \cdot g$. Obviously, the half-width of the resonance line is $\delta H = k\Delta H$, where the factor k (which is of the order of unity) is determined by the line shape. Thus, in our case formula (1) will be valid with $\gamma = k(\Delta g/g)$ a certain constant.

On the basis of the foregoing assumptions about the character of the EPR line broadening, we have calculated in this article the EPR line shape in samples containing paramagnetic complexes with random orientation and with an effective spin S = 1/2 and an axially-symmetrical g-tensor ($g_x = g_y = g_{\parallel}$, $g_z = g_{\perp}$). A comparison of the theoretical curves with the experimental data has enabled us to obtain the values of $g_{\parallel}$, $g_{\perp}$, and γ for the ions Ce^{3+}, Nd^{3+}, Dy^{3+}, and Yb^{3+}, introduced in a number of low-temperature glasses. From an analysis of these data we were able to establish certain general laws governing the symmetry of the local electric field of a paramagnetic complex containing rare-earth ions.

2. CALCULATION OF THE EPR LINE SHAPE AND ANALYSIS OF THE EXPERIMENTAL CURVES

According to[9], the intensity of the absorption line is equal to

$$J(H) = \int_{H_{\perp}}^{H_{\parallel}} \frac{f(H)\,(1 + H_{\parallel}^{-2}H'^2)\,dH'}{H'^2(H'^2 - H_{\perp}^2)^{1/2}} \quad \text{for } H_{\parallel} > H_{\perp}, \tag{2}$$

$$J(H) = \int_{H_{\parallel}}^{H_{\perp}} \frac{f(H)\,(1 + H_{\parallel}^{-2}H'^2)\,dH'}{H'^2(H_{\perp}^2 - H'^2)^{1/2}} \quad \text{for } H_{\perp} > H_{\parallel}, \tag{3}$$

where $H_{\parallel}$ and $H_{\perp}$ are the values of the magnetic field H corresponding to the orientations z ∥ H and z ⊥ H of the symmetry axis of the paramagnetic complex. Let us assume that the individual line has a Lorentz shape and consequently the shape function is given by

$$f(H) \sim \delta H \,/\, [(H - H')^2 + \delta H^2]. \tag{4}$$

The integrals (2) and (3) were calculated[1] under the assumption that δH is determined by formula (1). A com-

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[1] We note that the results of the calculations of the integrals (2) and (3), given in [9], apparently contain many misprints.

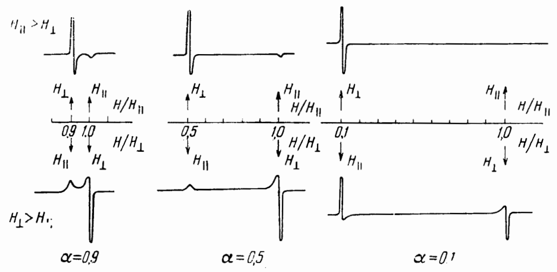

FIG. 1. EPR line shape calculated for different values of α at $\gamma = 0.003$.

puter yielded the theoretical curves for different values of γ and α (Figs. 1 and 2), where $\alpha = g_{\parallel}/g_{\perp}$ if $H_{\parallel} > H_{\perp}$, and $\alpha = g_{\perp}/g_{\parallel}$ if $H_{\parallel} < H_{\perp}$.

We have experimentally investigated more than 20 different rare-earth complexes at the frequencies $\nu_1 = 9500$ MHz, $\nu_2 = 900$ MHz, and $\nu_3 = 300$ MHz at $T = 4.2^{\circ}$K. The table lists the results of an analysis of the experimental data for some of the complexes investigated by us.

The good agreement observed at the center of the calculated and experimental lines, and the discrepancy between them on the wings (Fig. 3a) are apparently due to the fact that at the center the individual line is Lorentzian and on the wings it is Gaussian.

From a comparison of the theoretical and experimental curves it is possible to determine the values of α and γ. The parameter γ can be estimated with great accuracy, since a small change of γ has a noticeable effect on the shape of the curve (Fig. 3c). For greater reliability, the values of α and γ were obtained from the EPR spectrum measured at different frequencies. To determine γ at low frequencies it is necessary to choose spectra obtained with strongly diluted substances, with concentration $c \leq 0.06$ mole/l. In highly concentrated samples, unlikely large values of γ are obtained ($\gamma = 0.5$–0.7).

The crux of the matter is apparently the fact that in weak fields H the contribution to the width of the dipole-dipole interactions becomes predominant when the concentration of the paramagnetic ions increases.

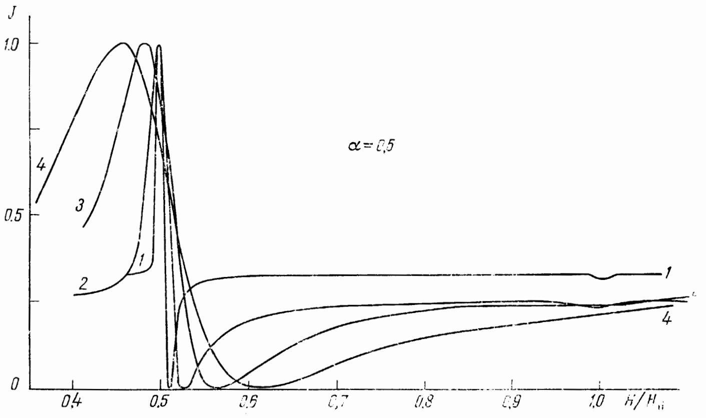

FIG. 2. EPR line shape calculated for α = 0.5 at different values of γ: 1) 0.003, 2) 0.03, 3) 0.1, 4) 0.2.

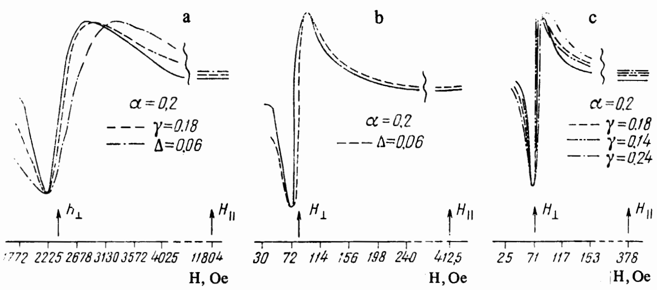

FIG. 3. Comparison of EPR lines of $NdCl_3 \cdot 6H_2O$ in alcohol (solid line) with the theoretical curves calculated in accordance with formula (4) for γ = 0.18, γ = 0.14, and γ = 0.24, and in accordance with the formulas of Ibers and Swalen [9] for $\Delta = (\delta H + \delta H_{\mathrm{dip}})/H_{\parallel} = 0.06$: a–$\nu$ = 9500 MHz, c = 0.5 mole/l; b–ν = 930 MHz, c = 0.5 mole/l; c–ν = 298 MHz, c = 0.06 mole/l.

To calculate the dipole broadening, we have used the formulas of Kittel and Abrahams[10], in which the second and fourth moments M_2 and M_4 are averaged over different directions of the magnetic field H. As applied to our case, M_2 and M_4 are given by

$$M_2 = \frac{c}{4h^2} \sum F_{jk}^2, \quad M_4 = \frac{c}{16h^4} \sum F_{jk}^4, \tag{5}$$

Sample number	Compound	Solvent	ν, MHz	$g_{\perp}$	$g_{\parallel}$	γ	δH dip, Oe (theor.)	δH dip, Oe (exp.)
1	$Ce(CNS)_3 \cdot 7H_2O$	Triethyl phosphate	9500 290	2,30±0,05 2,20±0,10	0,69±0.05 0.72±0,10	0,14 0,16	— 20	— 20
2	$CeCl_3 \cdot 6H_2O$	Tributyl phosphate	942 290	2,2±0.10 2.1±0,10	0,67±0.10 0,6±0,10	0,28 0,30	— —	— —
3	Ditto	Ethanol	940 290	1.9±0,10 2,0±0.10	0,76±0.10 0,76±0,10	0,70 0,70	— —	— —
4	Ditto	HCl 19%	266	2,3±0,10	0,92±0,10	0.60	—	—
5	$NdCl_3 \cdot 6H_2O$	Ethanol	9500 930 298	2,8±0.05 2,7±0,10 2,7±0,10	0,56±0.05 0,50±0.10 0,50±0,10	0,19 0,20 0,18	— — 20	— — 16
6	Ditto	HCl 19%	9500 960 282	2,8±1,05 2,8±0.10 2,8±0.10	0,6±0.05 0,6±0,1 0,6±0,10	0,24 0,24 0.22	— — 21	— — 22
7	$Nd(C_2H_3O_2)_3 \cdot H_2O$	Glycerin	9500 280	2,7±0,05 2,7±0,1	0,54±0.10 0,5±0.1	0,30 0,28	— —	— —
8	$Nd(CNS_3) \cdot 7H_2O$	Tributyl phosphate	9500 940 280	2.8±0,05 2.9±0,10 2.8±0,10	1,05±0.05 1,03±0.10 1,10±0,10	0,28 0,28 0,30	— — 20	— — 23
9	$DySO_4 \cdot 6H_2O$	Glycerin	290	6.9±0,10	1.4±0.10	0.45	—	—
10	$YbSO_4 \cdot 6H_2O$	Glycerin	290	4.2±0,10	1,26±0,10	0.40	—	—

where

$$F_{jk}^2 = 9g^4\beta^4/5r_{jk}^6, \quad \sum_k r_{jk}^{-6} = 8.5d^{-6}, \quad \sum_k r_{jk}^{-12} = 6.3d^{-12}.$$

Here r_{jk} is the distance between the paramagnetic centers j and k, and d is the minimum value of r_{jk}; for rare-earth ions in the glasses investigated by us, $d \approx (5-6) \times 10^{-8}$ cm[11].

In order to take into account the dipole broadening due to the protons, we used the Van-Vleck formula to calculate the moment M_2'[12].

It is well known[13] that the dipole-dipole interaction consists of static and dynamic parts. The dynamic broadening, which amounts to one half the static broadening, takes place only for equivalent paramagnetic centers. Since the glasses and solutions consist of nonequivalent paramagnetic complexes, the final expression for δH_{dip} must be divided by 3/2. Then the width of the individual line, due to the dipole-dipole interaction, is equal to

$$\delta H_{\text{дип}} = \rho\sqrt{M_2 + M_2'}, \quad \text{where } \rho = \frac{2\pi}{3\sqrt{3}}\frac{M_2}{M_4^{1/2}}. \tag{6}$$

In order to determine δH_{dip} from the spectra, we can use curves calculated in accordance with the formulas of Ibers and Swalen[9], since the dipole broadening does not depend on the magnitude of the magnetic field. As seen from Fig. 3b, their curves turned out to be perfectly suitable for the analysis of concentrated samples.

The experimentally determined values of δH_{dip} are in good agreement with the values calculated by formula (6) for concentrations c = 0.06–0.5 mole/l. The last columns of the table give the theoretical and experimental values of δH_{dip} for c = 0.5 mole/l.

It should be noted that the values of $g_{\parallel}$ and $g_{\perp}$, obtained at different concentrations from the curves of Ibers and Swalen, coincide with the g factors obtained by us from the high-frequency curves (see the table). The values of γ obtained from the high-frequency and low-frequency EPR spectra (at $c \le 0.6$ mole/l) are also in agreement (see the table and Fig. 3c).

3. SYMMETRY OF THE LOCAL ELECTRIC FIELD IN PARAMAGNETIC COMPLEXES

In explaining the spectra observed by us, we have assumed that the crystal field has an axial (tetragonal or trigonal) symmetry. Let us examine the extent to which this assumption is justified. We assume that the symmetry is much lower, and all three values of the g-factor (g_x, g_y, and g_z) differ greatly from one another. In single crystals, if the field H is directed along the x axis, then the intensity of the EPR line is proportional to $g_z^2 + g_y^2$. It is clear therefore that in disordered systems, in an EPR line with $g_x \ne g_y \ne g_z$, the more intense part should be the right part of the curve corresponding to the smallest component of the g tensor. However, in all the cases investigated by us, the left wing of the curve was more intense. The assumption that $g_x = g_y < g_z$, as seen from Fig. 1, undoubtedly contradicts the experimental data. Consequently, only one possibility agrees with our experiment, namely $g_x \approx g_y > g_z$. The fact that in most cases the theoretical curves calculated under the assumption of axial symmetry are in good agreement with the experimental ones only confirms our assumption. It should be noted that for samples No. 3 and 4 (see the table), exceedingly large values of γ were obtained; in all probability, the assumption $g_x = g_y$ is not valid for these samples.

In crystals with axial (tetragonal or trigonal) symmetry, the cases $g_{\parallel} > g_{\perp}$ and $g_{\perp} > g_{\parallel}$ are encountered with equal frequency. In high- and low-temperature glasses, for all the rare-earth ions investigated to date, we always have $g_{\perp} > g_{\parallel}$. This fact has a simple explanation if it is assumed that in the first approximation the field is "purely axial." In this case the off-diagonal matrix elements of the crystal field vanish and therefore the energy levels split into doublets $\pm J_z$, where $J_z = 1/2, 3/2, 5/2, \ldots J$. It is quite probable that the lower doublet is ± 1/2. The components of the g-factors are equal to[13]

$$g_{\parallel} = 2\langle + |J_z| + \rangle g_0, \quad g_{\perp} = 2\langle - |J_x| + \rangle g_0, \tag{7}$$

where g_0 is the Lande factor for the free ion.

It follows therefore that for the doublet ± 1/2

$$g_{\parallel} = g_0, \quad g_{\perp} = g_0\sqrt{J(J+1) + 1/4}. \tag{8}$$

We see that $g_{\perp} > g_{\parallel}$ always. According to (8), for the ions investigated by us we have

	Ce^{3+}	Nd^{3+}	Dy^{3+}	Yb^{3+}
$g_{\parallel}$	0,87	0,73	1,33	1.14
$g_{\perp}$	2,57	3,6	10	4,6

A comparison of these values of the g factors with the experimental ones reveals a sufficiently good agreement for most investigated ions (see the table). It is remarkable that the theoretically-predicted growth of the g-factor on going from one ion to the other coincides with the experimental one. One can hope that the best agreement between the theoretical and experimental values of $g_{\parallel}$ and $g_{\perp}$ will be attained if account is taken of the off-diagonal matrix elements of the electric field, as the result of which there are mixed with the wave functions $|\pm 1/2\rangle$ of the main Kramers doublet also states with $J_z > 1/2$. It is easy to show, using the Ce^{3+} ions, that if the local symmetry of the field is tetragonal, then the off-diagonal matrix elements vanish, independently of our assumption that the lower state is the ± 1/2 doublet. This conclusion becomes of particular interest if it is recalled that no local crystal fields of tetragonal symmetry were ever observed in hydrated rare-earth salts[14]. On the other hand, if the electric field has trigonal or rhombic symmetry, then good agreement between theory and experiment can be obtained.

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[1] T. S. Al'tshuler, Dokl. Akad. Nauk SSSR **174**, 549 (1967) [Sov. Phys.-Dokl. **5**, 481 (1967)].

[2] B. Bleaney, Proc. Phys. Soc. **A63**, 407 (1950); Phil. Mag. **42**, 441 (1951); Proc. Phys. Soc. **A75**, 621 (1960).

[3] R. H. Sands, Phys. Rev. **99**, 1222 (1955).

[4] F. K. Kneubuhl, J. Chem. Phys. **33**, 1074 (1960).

[5] J. W. Searl, R. C. Smith, and S. J. Wyard, Proc. Phys. Soc. **A74**, 491 (1959).

[6] A. K. Chirkov, A. A. Kokin, Zh. Eksp. Teor. Fiz. **39**, 1381 (1960) [Sov. Phys.-JETP **12**, 964 (1960)].

[7] Ya. S. Lebedev, Zh. strukt. khim. 4, 22 (1963).

[8] V. S. Korol'kov and A. K. Potapovich, Opt. Spektrosk. 16, 461 (1964).

[9] J. A. Ibers and J. D. Swalen, Phys. Rev. **127**, 1914 (1962).

[10] C. Kittel and E. Abrahams, Phys. Rev. 90, 238 (1953).

[11] F. H. Spedding and J. S. Yaffe, J. Amer. Chem. Soc. **74**, 19, 47, 51 (1952); F. H. Spedding, P. E. Porter, and J. M. Wright, J. Am. Chem. Soc. **74**, 11, 2778 (1952).

[12] J. H. Van-Vleck, Phys. Rev. **73**, 1249 (1948).

[13] S. A. Al'tshuler and B. M. Kozyrev, Elektronnyĭ paramagnitnyĭ rezonans (Electron Paramagnetic Resonance), Fizmatgiz, 1961.

[14] K. H. Hellwege and H. C. Kahle, Z. Physik **129**, 62 (1950).

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