THE SHAPE OF THE ELECTRON RESONANCE LINE IN A SYSTEM OF PARTICLES WITH AN ANISOTROPIC g FACTOR

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The moments and the line shape are calculated for a system of randomly oriented noninteracting particles with an anisotropic g factor, for the case of no thermal motion. The results of the calculation are compared with experimental data on resonance absorption in powders, glasses, and undercooled solutions.

1. In observations of electron magnetic resonance in powders, glasses, solid solutions, undercooled solutions, and so on, one finds at sufficiently high frequencies a considerable distortion of the shape of the absorption line, which is caused by the manifestation of anisotropy of the g factors of the individual particles and of the hyperfine structure constant.[1-3]

A characteristic feature of the distortions caused by anisotropy of the g factor is an increase of the asymmetry of the line with increase of the magnetic field. The distortions of the line shape that appear because hyperfine structure shows up in sufficiently strong magnetic fields do not depend on the strength of the field.

There have been a number of papers[4,5] on the analysis of the effect of the anisotropy of the g factor of the randomly oriented particles on the line shape of magnetic resonance in glasses and organic compounds. These papers, however, have dealt only with a uniaxial anisotropy of the g factor.

The unsymmetrical character of the absorption line in a powder of the free organic radical diphenyl-picryl hydrazyl (DPPH) has been observed experimentally at the frequency 25,500 Mc/sec.[6]

An attempt to explain the observed asymmetry of the line by the presence of a uniaxial anisotropy of the g factor of the individual single crystals has been made in a paper by Kikuchi and Cohen.[7] In calculating the line shape they used results obtained by measurements of the g factor made with individual, relatively large, single crystals of DPPH. Lack of the necessary experimental data prevented these authors from making a comparison of theory with experiment.

A temperature dependence of the anisotropy of the g factor of a single crystal of DPPH has been discovered by Singer and Kikuchi.[8]

In such complicated paramagnetic compounds as free organic radicals it is natural to expect that there will be not uniaxial, but triaxial anisotropy.[9] In this case the shape of the absorption line can be still more complex.

In the present paper the moments and the line shape are calculated for a system consisting of particles that have a weak triaxial or uniaxial anisotropy of the g factor and are randomly oriented in space.

2. The absorption spectrum of electronic magnetic resonance in a specimen with anisotropy of the g factor is determined by the eigenvalues of the spin Hamiltonian

$$\mathcal{H} = \mu_0 (\mathbf{S g H_0}), \qquad (1)$$

where μ_0 is the Bohr magneton. In its principal axes the tensor $\mathbf{g}$ has the components $g + \Delta g_i$ ($i = 1, 2, 3$), where g is the average value, so that

$$\Delta g_1 + \Delta g_2 + \Delta g_3 = 0.$$

We shall assume that the internal interactions lead only to a broadening of the spectrum lines.

If the external magnetic field H_0 is directed along the z axis, then for an arbitrary orientation of the particle relative to the external field the expression (1) takes the form

$$\mathcal{H} = \mu_0 H_0 (g_{xz}\hat{S}_x + g_{yz}\hat{S}_y + g_{zz}\hat{S}_z). \qquad (2)$$

In the case of small anisotropy, $\Delta g_{1,2,3} \ll g$, the nondiagonal terms g_{xz}, g_{yz} can be neglected in first approximation, and the component g_{zz} of the tensor $\mathbf{g}$ can be represented in the form

$$g_{zz}(\vartheta, \varphi, \psi) = g + \Delta g_{zz}(\vartheta, \varphi, \psi), \qquad (3)$$

where ϑ, φ, ψ are the Euler angles that determine the orientation of the principal magnetic axes of

the particle relative to a fixed coordinate system.

The quantity $\Delta g_{zz} (\vartheta, \varphi, \psi)$ is calculated from

$$\Delta g_{zz} (\vartheta, \varphi, \psi) = (\mathbf{A}^{-1} \Delta \mathbf{g} \mathbf{A})_{zz},$$

where $\Delta \mathbf{g}$ is the anisotropic part of the tensor in the system of the principal axes and $\mathbf{A}$ is the matrix of the rotation of the principal axes of the particle relative to the coordinate system; we get as the result

$$\Delta g_{zz} = \Delta g_1 \sin^2 \vartheta \sin^2 \psi + \Delta g_2 \sin^2 \vartheta \cos^2 \psi + \Delta g_3 \cos^2 \vartheta. \quad (4)$$

We now find as the expression for the resonance frequency

$$\overset{*}{\omega_0} = \mu_0 g_{zz} H_0 / \hbar = \omega_0 + \frac{\mu_0 H_0}{\hbar} \Delta g_{zz}(\vartheta, \varphi, \psi), \quad (5)$$

where $\omega_0 = \mu_0 g H_0 / \hbar$.

For comparison with the experimental data it is convenient to express this result in field units:

$$\overset{*}{H_0} = H_0 + \Delta H_1 \sin^2 \vartheta \sin^2 \psi + \Delta H_2 \sin^2 \vartheta \cos^2 \psi$$

$$+ \Delta H_3 \cos^2 \vartheta = H_0 + \Delta H_z, \quad (6)$$

where $\Delta H_i = \Delta g_i H_0 / g$. The values of the anisotropy constants ΔH_i can be determined from the displacement of the maxima of the resonance absorption lines for three independent rotations of a single crystal around its principal axes ($\vartheta = \pi/2$, $\psi = 0$, $\psi = \pi/2$) in the plane perpendicular to the direction of the external magnetic field.

3. On the assumption that the orientations of the individual particles are randomly distributed in space, the total shape of the absorption line can be found by averaging the spectra of the individual particles over all possible directions:

$$J (H - H_0) = \frac{1}{\pi} \int_0^{\pi/2} \sin \vartheta \, d\vartheta \int_0^{\pi} d\psi I (H - \overset{*}{H_0}), \quad (7)$$

where $I(H - \overset{*}{H_0})$ is the function, normalized to unity, for the line shape of the individual particle, which can be represented in the form

$$I (H - \overset{*}{H_0}) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} G (t) \exp \{i (H - \overset{*}{H_0}) t\} \, dt. \quad (8)$$

Then

$$J (H - H_0) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \mathfrak{G} (t) \exp \{i (H - H_0) t\} \, dt, \quad (9)$$

$$\mathfrak{G} (t) = \frac{1}{\pi} \int_0^{\pi/2} \sin \vartheta \, d\vartheta \int_0^{\pi} d\psi \, G (t) \exp \{i (H - \overset{*}{H_0}) t\} \, dt. \quad (10)$$

To find the moments of the line shape we expand the expression for the function $G(t)$, which is obtained from Eq. (8) by the inverse Fourier transformation, in a power series in t. Comparing the coefficients of identical powers of t, we get

$$M_n = \int_{-\infty}^{+\infty} I (x) x^n \, dx = (- i)^n \frac{d^n}{dt^n} G (0). \quad (11)$$

Here M_n are the moments of the absorption line for the individual particle relative to the field $\overset{*}{H_0}$. In a similar way we can determine the moments of the total absorption curve relative to the field H_0

$$\mathfrak{M}_n = \int_{-\infty}^{+\infty} J (x) x^n \, dx = (- i)^n \frac{d^n}{dt^n} \mathfrak{G} (0). \quad (12)$$

Assuming that the absorption line for the individual particle is symmetrical and that its shape does not depend on the orientation, by using Eqs. (10) and (12) we find

$$\mathfrak{M}_0 = 1, \qquad \mathfrak{M}_1 = 0, \qquad \mathfrak{M}_2 = M_2 + \overline{\Delta H_z^2},$$

$$\mathfrak{M}_3 = - \overline{\Delta H_z^3}, \qquad \mathfrak{M}_4 = M_4 + 6 \overline{\Delta H_z^2} M_2 + \overline{\Delta H_z^4}, \quad (13)$$

where

$$\overline{\Delta H_z^n} = \frac{1}{4\pi} \int (\Delta H_z)^n \sin \vartheta \, d\vartheta \, d\varphi. \quad (14)$$

We have

$$\overline{\Delta H_z^2} = \frac{1}{5} (\Delta H_1^2 + \Delta H_2^2 + \Delta H_3^2)$$

$$+ \frac{2}{15} (\Delta H_1 \Delta H_2 + \Delta H_1 \Delta H_3 + \Delta H_2 \Delta H_3),$$

$$\overline{\Delta H_z^3} = \frac{1}{7} (\Delta H_1^3 + \Delta H_2^3 + \Delta H_3^3) + \frac{3}{35} (\Delta H_1^2 \Delta H_2 + \Delta H_1 \Delta H_2^2$$

$$+ \Delta H_1^2 \Delta H_3 + \Delta H_3^2 \Delta H_1$$

$$+ \Delta H_2^2 \Delta H_3 + \Delta H_2 \Delta H_3^2) + \frac{2}{35} (\Delta H_1 \Delta H_2 \Delta H_3),$$

$$\overline{\Delta H_z^4} = \frac{1}{9} (\Delta H_1^4 + \Delta H_2^4 + \Delta H_3^4) + \frac{4}{63} (\Delta H_3^3 \Delta H_1$$

$$+ \Delta H_3 \Delta H_1^3 + \Delta H_2^3 \Delta H_1 + \Delta H_1^3 \Delta H_2 + \Delta H_2^3 \Delta H_3$$

$$+ \Delta H_3^3 \Delta H_2) + \frac{2}{35} (\Delta H_1 \Delta H_2 \Delta H_3^2$$

$$+ \Delta H_1 \Delta H_2^2 \Delta H_3 + \Delta H_1^2 \Delta H_2 \Delta H_3). \quad (15)$$

The presence of odd moments ($\mathfrak{M}_3 \neq 0$) is evidence of the unsymmetrical character of the total absorption curve.

To obtain the function for the shape of the total absorption curve we assume that the absorption curve of the individual particle has the Lorentz shape:

$$I (H - \overset{*}{H_0}) = \frac{1}{\pi \Delta H} \left[\left(\frac{H - \overset{*}{H_0}}{\Delta H} \right)^2 + 1 \right]^{-1}, \quad (16)$$

where ΔH is the half-width of the line.

Substituting this expression in Eq. (7) and integrating over $d\vartheta$, we get

$$J (H - H_0) = \frac{1}{2\pi^2 \Delta H} \int_0^{\eta} d\psi \left\{ \frac{1}{\gamma} \left[\frac{1}{2\alpha} \ln \frac{\beta + \gamma + \alpha}{\beta + \gamma - \alpha} \right.\right.$$

$$\left.\left. + \frac{1}{p} \left(\tan^{-1} \frac{2\beta + \alpha}{p} + \tan^{-1} \frac{2\beta - \alpha}{p} \right) \right\}, \quad (17)$$

$$\alpha = \left[2\beta\left(\gamma - \frac{H - H_0}{\Delta H} + \beta + \frac{2}{3}\frac{\Delta H_3 - \Delta H_1}{\Delta H}\right)\right]^{1/2},$$

$$\gamma = \pm\left[1 + \left(\frac{H - H_0}{\Delta H} - \beta - \frac{2}{3}\frac{\Delta H_3 - \Delta H_1}{\Delta H}\right)^2\right]^{1/2},$$

$$p = \sqrt{4\beta\gamma - \alpha^2}, \qquad \beta = \frac{\Delta H_1 - \Delta H_3 + (\Delta H_1 - \Delta H_2)\cos^2\psi}{\Delta H}. \tag{18}$$

The upper sign is for $\beta > 0$ and the lower for $\beta < 0$. In the general case the further integration can be accomplished only by numerical methods.

To determine the function for the shape of the total absorption curve when the anisotropy of the hyperfine structure constant is taken into account we must make the replacements

$$H_0 \to H_0 + Am, \quad \Delta H_i \to \Delta H_i + \Delta A_i m \tag{19}$$

in the expression (17). Thus in this case the change of intensity of the individual components of the hyperfine structure follows a law analogous to that for the change of the intensity of the absorption line owing to the existence of an anisotropy of the g factors of the individual particles.

From the results given in the paper of Kikuchi and Cohen,[7] which were obtained for a single crystal of the organic free radical carbazyl, it follows that for rotations of the crystal around the magnetic symmetry axes in a field $H_0 = 8000$ oe

$$\Delta H = 0.25 \text{ oe}, \qquad \Delta H_1 - \Delta H_2 = -2.4 \text{ oe},$$

$$\Delta H_1 - \Delta H_3 = 3.6 \text{ oe}, \qquad \Delta H_2 - \Delta H_3 = 6.0 \text{ oe}, \tag{20}$$

and the hyperfine structure is not manifested here. Unfortunately from the paper in question we cannot establish the direction of the axes with sufficient accuracy.

The results of a numerical integration of Eq. (17) are shown in Fig. 1.
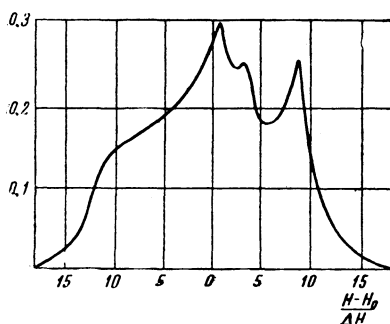
FIG. 1. The function for the shape of the total absorption curve in the case of triaxial anisotropy of the g factor. The numerical integration was performed with the values (20); the quantity plotted as ordinate is $J(H-H_0)\Delta H\cdot 5$.

A small difference in the magnetic properties of the individual particles, caused by defects of the crystal lattice,[2] can lead to a smoothing out of the shape of the total curve. This is evidently the explanation of the absence of distinct maxima of this sort on the experimental curves for polycrystalline specimens of free radicals.

Observations of the resonance absorption of

complicated complex ions Cu^{++} in undercooled solutions actually give curves analogous to that shown in Fig. 1,[10] owing to the identity of the individual molecules.

In the case of axial symmetry $\Delta H_1 = \Delta H_2 = -\Delta H_3/2$. Then after integrating the expression (17) we get

$$J(H - H_0) = \frac{1}{2\pi\Delta H\gamma}\left[\frac{1}{2\alpha}\ln\frac{\beta + \gamma + \alpha}{\beta + \gamma - \alpha}\right.$$

$$\left. + \frac{1}{p}\left(\tan^{-1}\frac{2\beta + \alpha}{p} + \tan^{-1}\frac{2\beta - \alpha}{p}\right)\right], \tag{21}$$

where α, β, γ are defined in Eq. (18) and $\beta = 3\Delta H_1/\Delta H$. Curves drawn for various values of β are shown in Fig. 2. This shape of the absorption curves is characteristic of glasses, undercooled solutions, and so on, whose paramagnetic complexes possess symmetries close to the axial type.[1,3,4]

FIG. 2. The function for the shape of the total absorption curve in the case of uniaxial anisotropy of the g factor, for various values of the parameter $\beta = 3\Delta H_1/\Delta H$; the quantity plotted as ordinate is $J(H-H_0)\Delta H\cdot 10$.
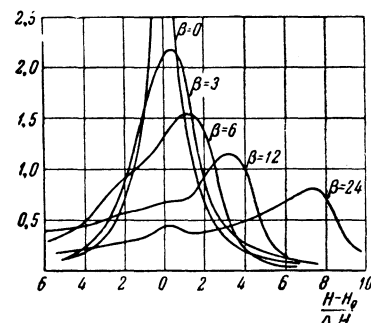
Both in the case of uniaxial anisotropy and in that of triaxial anisotropy the position of the main maximum is shifted relative to the position that corresponds to weak fields.

In strong fields the absorption curve has supplementary maxima in addition to the main maximum (Fig. 2). In weak fields the curve has a single maximum, whose position corresponds to the isotropic part of the g factor.

4. The widths and shapes of the resonance absorption curves for the free organic radicals (XC_6H_4) $(C_6H_5)N - NC_6H_2(NO_2)_3$, DPPH$(X = H)$, ClPPH$(X = Cl)$, and carbazyl $(C_6H_4)(C_6H_4)N - NC_6H_2(NO_2)_3$,[11] in powder form, have been studied in the low-frequency range, 9 Mc to 800 Mc, by means of the method described in references 12 and 13.

The width and shape of the absorption curve at frequencies 10,000 and 36,000 Mc were determined by means of videospectroscopes with resonators of the pass-band type. The absorption curves were photographed from the screen of the oscilloscope. The magnetic field was modulated at low frequency and amplitudes up to 200 oe. Nuclear resonance was used for the measurement and stabilization of the magnetic field.

The specimen was placed in the central part of a resonator oscillating in the H_{011} mode and could be turned around one of the axes.

The results of the measurements showed that the width and shape of the absorption curve in the low-frequency region is practically independent of the strength of the constant field, and in weak fields, for all the radicals studied, the width is the same as that of the absorption line of an individual single crystal.

It can be seen from the curves of Fig. 2 that as the field is increased the line width increases; at the same time the curve becomes more asymmetrical. A similar phenomenon is also observed in the case of triaxial anisotropy.

The experimental dependence of the line width on the constant magnetic field for a number of organic free radicals, which is shown in Fig. 3, can be satisfactorily explained on the basis of the anisotropy of the g factors of the individual single crystals.
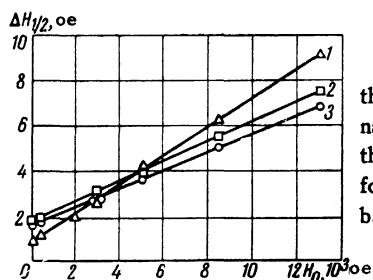

FIG. 3. Dependence of the half-width of the resonance absorption curve on the constant magnetic field for free radicals: 1 – carbazyl, 2 – ClPPH, 3 – DPPH.

Thus in the analysis of the data on the width and shape of the absorption lines in powders, glasses, solid solutions, undercooled solutions, etc., in the case of strong fields ($H_0 > 1000$ oe) one must take into account the fact that a considerable part of the line width is caused by the anisotropy of the g factor. But the considerations we have given about the effect of the anisotropy of the g factor of the individual particle on the shape of the line are not always taken into account. For example, in references 14 and 15 analyses of the shape of the absorption line in strong fields for powders of free radicals are made the basis of unconvincing de-

ductions about the effect of various substituted atoms on the size of the exchange interactions.

In a paper by Singer and Kikuchi[8] it has been found that with decrease of the temperature there is an increase of the absorption line width and of the anisotropy constants in an individual single crystal of DPPH, and also an increase of the absorption line width for a polycrystalline specimen in a strong field (8000 oe). The temperature dependence of the absorption line in the powder also gives evidence of the important part played by the anisotropy of the g factor of the individual particles.

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