

VERIFICATION OF THE FORM OF HIGH-FREQUENCY SUSCEPTIBILITIES AND THE SPECTRAL LINE OF THE GAUSSIAN TYPE

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In the present paper there are determined the shape of the high-frequency (HF) susceptibilities and the form of the spectral gaussian type line. It is based on the results of the authors of [2, 3], a vector model of magnetic resonance and it is shown that the component of the HF susceptibility κ' and the shape of the saturation term agree with the result which we obtain from the quantum mechanical description of the absorption of the HF energy and the components κ' , κ'' disturb the Kramers-Kronig relations. Further there is derived the shape of the spectral line in the absorption and the differential record and these shapes are compared with the information on the central moments according to [7] and with the experimental spectrum of the active coal spectrum EPR and polypropylene spectrum NMR.

ПРОВЕРКА ФОРМЫ ВЫСОКОЧАСТОТНОЙ МАГНИТНОЙ ВОСПРИИМЧИВОСТИ И СПЕКТРАЛЬНОЙ ЛИНИИ ГАУССОВСКОГО ТИПА

В работе определены форма высокочастотной магнитной восприимчивости и форма спектральной линии гауссовского типа. Векторная модель магнитного резонанса основана на результатах авторов, причем показано, что составляющая высокочастотной магнитной восприимчивости κ' и форма члена насыщения согласуются с результатом, который был получен, исходя из квантово-механического описания поглощения высокочастотной энергии. Составляющие κ' , κ'' нарушают соотношения Крамера-Кронига. Кроме того, определены формы линии спектра поглощения при помощи разных способов, и эти формы сравниваются с данными о центральных моментах инерции согласно [7] и с экспериментальными данными о ЭПР-спектре активного угля и НМР-спектре полипропилена.

1. INTRODUCTION

In a vector model describing the phenomenon of magnetic resonance of a paramagnetic material NMR, EPR the motion of the magnetic polarization vector is investigated in a simultaneous action of a static and an HF magnetic field.

In literature there are known differential equations describing the motion of the magnetic polarization vector with relaxation phenomena, where a stationary solution enables us to define the HF susceptibility of the Lorentzian [1] and the gaussian type simultaneously [2]. In paper [2] it is shown that the dispersion κ' and the absorption κ'' component of HF susceptibility of the gaussian type are

$$\kappa' = -\frac{1}{2} \kappa T_2^2 \omega_0 \Delta\omega P(a) \frac{1}{s+1} \exp \left[-\frac{1}{2} T_2^2 \Delta\omega^2 \right] \quad (1)$$

$$\kappa'' = \frac{1}{2} \sqrt{\frac{\pi}{2}} \kappa T_2 \omega_0 \frac{1}{s+1} \exp \left[-\frac{1}{2} T_2^2 \Delta\omega^2 \right] \quad (2)$$

where κ is the value of the static susceptibility of the samples, T_2 is the constant of the transversal relaxation, $\Delta\omega = \omega - \omega_0$ is the change of the frequency,

$$P(a) = \sum_{n=0}^{\infty} \frac{a^{2n}}{(2n+1) \cdot n!}$$

$$a = \frac{\sqrt{2}}{2} T_2$$

$$s = \frac{1}{2} \sqrt{2} \pi \omega_1^2 T_1 T_2 \exp \left[-\frac{1}{2} T_2^2 \Delta\omega^2 \right] \quad (3)$$

s is the saturation term, T_1 is the constant of the longitudinal relaxation, $\omega_1 = \gamma B_1$, γ is the gyromagnetic ratio of resonating elements, B_1 is the amplitude of the HF magnetic field and $n = 0, 1, 2, \dots$ is a whole positive number.

In current spectrometers the discharge is usually a condition of weak saturation $s \ll 1$ and therefore the saturation effect is neglected. In this case HF susceptibilities of the gaussian type are

$$\kappa' = -\frac{1}{2} \kappa T_2^2 \omega_0 \Delta\omega P(a) \exp \left[-\frac{1}{2} T_2^2 \Delta\omega^2 \right] \quad (4)$$

$$\kappa'' = \frac{1}{2} \sqrt{\frac{\pi}{2}} \kappa T_2 \omega_0 \exp \left[-\frac{1}{2} T_2^2 \Delta\omega^2 \right] \quad (5)$$

The intensity of the spectral curve of the gaussian type in the absorption shape is according to [2]

$$I(\omega) = \frac{2}{\mu_0} \omega_0 B_1^2 \kappa'' \quad (6)$$

where μ_0 is the permeability of vacuum.

In the present paper we shall show that the relations (2), (3) are in agreement

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with the results obtained by the quantum mechanical description of intensity of the spectral line and saturation and that the relations (4), (5) disturb the Kronig-Kramers relations. Concluding we present the experimental verification of the shape of the spectral line of the gaussian type.

II. CALCULATION OF κ'' AND THE SATURATED TERM FROM THE ENERGY ABSORPTION

The description of the absorption HF energy in the material from the point of quantum mechanics assumes that the amplitude of the induction of an HF magnetic field is contrary to the induction of a static field very small ($B_1 \ll B_0$) and therefore we used the method of the perturbation theory. From such a calculation it follows that the intensity of spectral line of the gaussian type where the absorbed power per unit volume is (see equation [4, 5])

$$I(f) = \frac{1}{2\mu_0} \kappa_0 \omega_0^2 B_1^2 \frac{1}{s+1} g(f) \quad (7)$$

where $f = \omega/2\pi$ is the linear frequency, $g(f)$ is a normalized function of the form of spectral line with the dimension of time, which satisfies the condition

$$\int_{-\infty}^{\infty} g(f) df = 1 \quad (8)$$

and s is a saturation term in the form

$$s = \frac{1}{2} T_1 \omega_0^2 g(f). \quad (9)$$

The normalized condition (8) is satisfied by a suitable gaussian function

$$g(f) = \sqrt{2\pi} T_2 \exp \left[-\frac{1}{2} T_2^2 (2\pi \Delta f)^2 \right]. \quad (10)$$

If we substitute eq. (10) into eq. (7) and we compare with eq. (6), setting $\Delta\omega = 2\pi \Delta f$, we obtain the formula

$$\kappa'' = \frac{1}{2} \sqrt{\frac{\pi}{2}} \kappa_0 T_1 \omega_0 \frac{1}{s+1} \exp \left[-\frac{1}{2} T_2^2 \Delta\omega^2 \right],$$

which is in agreement with eq. (2). Similarly, if we substitute eq. (10) into eq. (9), we obtain for the saturation term the formula

$$s = \frac{1}{2} \sqrt{2\pi} \omega_0^2 T_1 T_2 \exp \left[-\frac{1}{2} T_2^2 \Delta\omega^2 \right],$$

which is in agreement with eq. (3).

III. KRONIG-KRAMERS RELATIONS

The direct calculation of the dispersion by means of the perturbation theory is unrealizable. In practice, we can compute from the absorption energy the high frequency component of the susceptibility κ'' , then we can compute by means of Kronig-Kramers relations the dispersion component κ' . This procedure is possible because between the cause (the magnetic induction) and its consequence (the magnetic polarization) there exists the time causality, which we can express mathematically by means of linear formulas. In the frequency spectrum it means that between the magnetic induction and the magnetic polarization there always exists the displaced phase, which we can describe by means of the complex coefficient proportion between them. This complex number will be called the complex susceptibility, the real part of which expresses the dispersion, while its imaginary part expresses the absorption. The Kronig-Kramers relation for the dispersion (see for example [5, 6]) is

$$\kappa'(\omega) - \kappa'(\infty) = \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\kappa''(\omega')}{\omega' - \omega} d\omega'$$

where $\kappa'(\infty)$ is the value of the dispersion if $\omega \rightarrow \infty$, which is equal to zero and the symbol \mathcal{P} stands for the principal part of the integral, that is

$$\kappa'(\omega) = \frac{1}{\pi} \left\{ \lim_{\epsilon \rightarrow 0} \int_{-\infty}^{\omega-\epsilon} \frac{\kappa''(\omega')}{\omega' - \omega} d\omega' + \lim_{\epsilon \rightarrow 0} \int_{\omega+\epsilon}^{\infty} \frac{\kappa''(\omega')}{\omega' - \omega} d\omega' \right\}.$$

Substituting κ'' from formula (5) and by setting $\omega' - \omega = x$, $d\omega' = dx$, $\Delta\omega' = x + \Delta\omega$, we obtain in integrands the expression $\exp[-x\Delta\omega T_2^2]$, which we developed in an infinite series. When we multiply an infinite series with the remaining part of the integrand, we obtain by the arrangement Poisson's integrals, of which the non-zero values have only the expression (see [3])

$$\lim_{\epsilon \rightarrow 0} \left\{ \int_{-\infty}^{-\epsilon} x^{2n} e^{-\alpha x^2} dx + \int_{\epsilon}^{\infty} x^{2n} e^{-\alpha x^2} dx \right\} = \frac{1.3.5 \dots (2n+1)}{2^n} \sqrt{\frac{\pi}{\alpha^{2n+1}}}$$

where $\alpha = \frac{1}{2} T_2^2$ and $n = 0, 1, 2, \dots$ is a whole positive number. By the next arrangement we obtain the formula

$$\kappa'(\omega) = -\frac{1}{2} \kappa_0 \omega_0 \Delta\omega T_2^2 P(a) \exp \left[-\frac{1}{2} T_2^2 \Delta\omega^2 \right]$$

where

$$P(a) = \sum_{n=0}^{\infty} \frac{a^{2n}}{(2n+1)n!}$$

and $a = \frac{\sqrt{2}}{2} T_2$,

which is in agreement with the expression of the dispersion part of the susceptibility $\chi''(\omega)$, which has been derived from the motion equations of the polarization vector and is expressed in formula (4).

IV. CENTRAL MOMENT OF THE ABSORPTION LINE

When we investigate paramagnetic samples by means of resonance methods, absorption of the HF energy in the samples takes place. The intensity of the spectral line is then determined by relation (6). In practice it is more advantageous

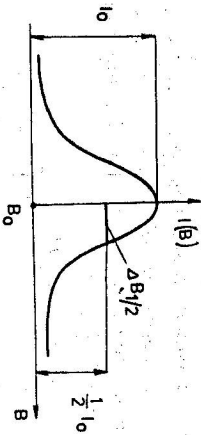


Fig. 1.

if the frequency of the HF magnetic field is constant and the magnitude of the static magnetic field varies. In that case the relation (6) can be expressed as a function of the magnetic field induction in the form (see [3])

$$I(B) = I_0 \exp \left[-\frac{(B - B_0)^2}{\Delta B_{1/2}^2} \ln 2 \right] \quad (11)$$

where I_0 is the value of $I(B)$ in the case of $B = B_0$ and $\Delta B_{1/2}$ is the half-width of the line at half-height (see Fig. 1). Simultaneously

$$I_0 = \frac{1}{\mu_0} \sqrt{\frac{\pi}{2}} \kappa T_2 \gamma^2 B_0^2 B^2$$

$$\Delta B_{1/2} = \frac{1}{T_2 \gamma} \sqrt{2 \ln 2}$$

The central n th moment of the absorption line is

$$M_n = \frac{\int_{-\infty}^{\infty} I(B)(B - B_0)^n dB}{\int_{-\infty}^{\infty} I(B) dB} \quad (12)$$

Van Vleck [7] proved that the half-width at half-height, the second moment M_2^s

and the fourth moment M_4 of the gaussian absorption line fulfil the relations $\Delta B_{1/2} = 1.175 M_2^s$, $M_4/M_2 = 1.32$. After substituting (11) into (12) we obtained the following relations: $\Delta B_{1/2} = 1.177 M_2^s$, $M_4/M_2 = 1.316$. These relations are in very good agreement with the data of Van Vleck.

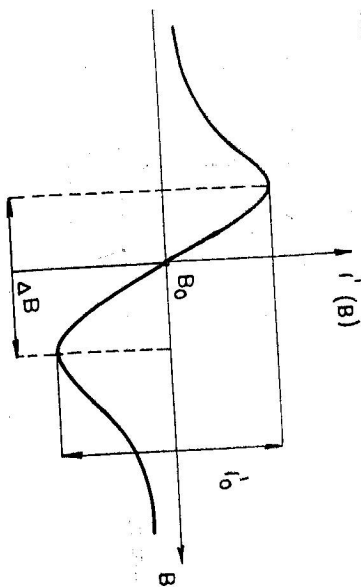


Fig. 2.

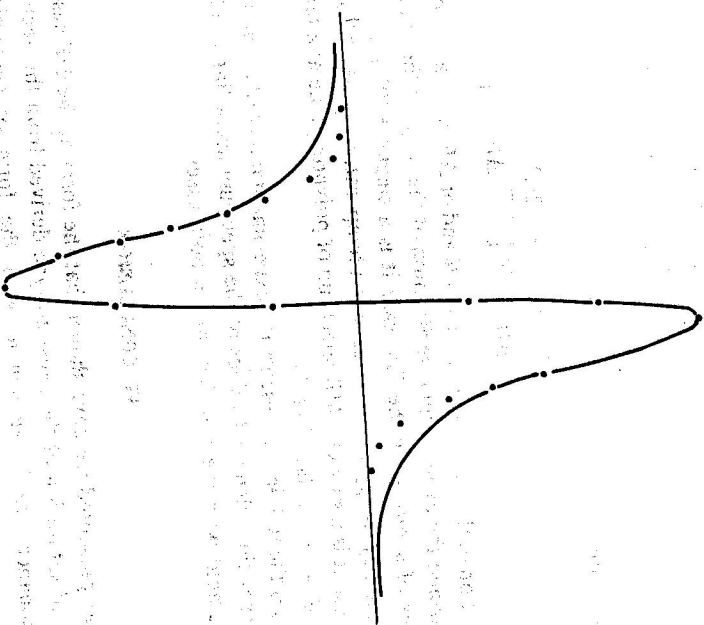


Fig. 3.

V. EXPERIMENTAL VERIFICATION OF THE FORM OF THE SPECTRAL LINE

At present the spectrometers do not register the absorption spectrum in the form (11), but in the form of its first derivative $I'(B) = dI(B)/dB$ which is plotted in Fig. 2.

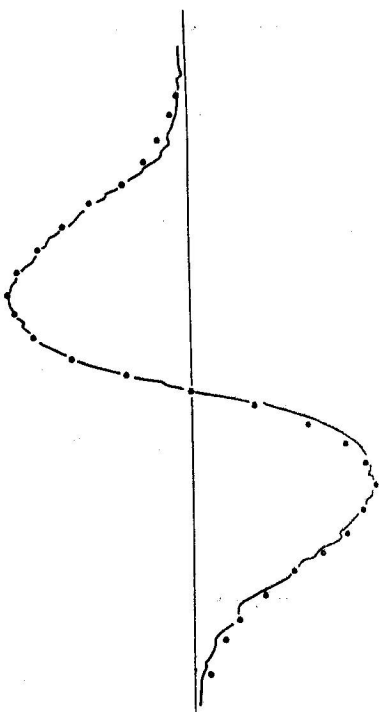


Fig. 4.

After calculation

$$I'(B) = I_0 \sqrt{e} \frac{B - B_0}{\Delta B^2} \exp \left[-\frac{2(B - B_0)^2}{\Delta B^2} \right]. \quad (13)$$

The explanation of the new line parameters I_0 and of ΔB is evident from Fig. 2.

We performed the experimental verification of the form of the spectral line (13) on two types of samples. In the first case it is a singlet EPR spectrum of a free radical obtained by the pyrolysis of sugar at a temperature of 400 °C (see Fig. 3). In the second case it is a singlet NMR spectrum of polypropylene at a temperature of the sample of — 62 °C (see Fig. 4).

In both cases the full line represents the experimental record of the spectrum, the points represent the calculated values of the spectrum according to (13). There is a good agreement with the gaussian line in both cases.

VI. CONCLUSION

In the paper presented we have shown that the form of the HF susceptibilities and the form of saturation of the gaussian type derived from the vector model of magnetic resonance are in agreement with the form of susceptibilities and saturation obtained from a quantum mechanics description of magnetic resonance

phenomena. We have shown that the HF susceptibilities of the gaussian type satisfy the relations. The form of the absorption spectrum together with its derivation form have been derived. We have shown that the half-width at the half-height of the absorption spectrum $\Delta B_{1/2}$ and the second central moment M_2 are in relation $\Delta B_{1/2} = 1.777 M_2$ and the quotient of the fourth M_4 and the second M_2 central moment is 1.316, which is in very good agreement with Van Vleck's data [7]. The experimental verification of the form of the spectral line in the derivation record for the free radical of active coal (spectrum EPR) and polypropylene (spectrum NMR) is in conformity with the calculated values.

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