Low-temperature theory of the magnetic-resonance lineshape in the memory-function formalism

L. L. Buishvili,[1)] M. D. Zviadadze,[2)] and É. Kh. Khalvashi

Batum Affiliate of the Georgian Technical University

(Submitted 19 October 1991)
Zh. Eksp. Teor. Fiz. **101**, 1295–1299 (April 1992)

Using an extension of the memory-function method to the case of low temperatures, we derive an analytical expression for the curve of the magnetic-resonance absorption line. The expression takes into account the first four moments of the lineshape. The results are in good agreement with experiment.

1. INTRODUCTION

The low-temperature theory, based on the method of moments, of the shape of a magnetic-resonance absorption line appeared in the 1950s and basically reduced to calculating the corresponding moments of the resonance line.[1–3] The first three moments for the EPR line[1,2] and the first moments for the NMR line (Ref. 3, Vol. 2) were calculated. It was shown experimentally and theoretically semiqualitatively that as the temperature decreases the EPR line narrows and becomes asymmetric, irrespective of its shift[1,2] (in the case of a cubic lattice with zero first moment the third moment was found to be nonzero). The same thing was observed in the case of NMR on ^{19}F-nuclei in CaF_2, where the shape of the resonance line transformed with increasing polarization of the nuclei from Gaussian to Lorentzian (Ref. 3, Vol. 2). We note that when the method of moments is applied in both the high- and low-temperature regions the lineshape is judged according to the ratio M_4/M_2^2, where M_2 and M_4 are the second and fourth moments of the resonance line: if $M_4/M_2^2 = 3$ holds, the line is considered to be Gaussian and its width is determined only by the second moment M_2; if, however, we have $M_4/M_2^2 \gg 3$, the line is considered to be Lorentzian and its width is determined by both the second and fourth moments. As a rule, however, for specific materials the ratio M_4/M_2^2 is never exactly equal to 3 and it is obvious that even in the case of a Gaussian shape, apart from M_2, higher order moments should also contribute to the linewidth. In addition, it is impossible to obtain an analytical expression for the lineshape with the help of the method of moments and, correspondingly, it is impossible to compare with experiment. It is in this connection that a theory giving an analytical expression for the lineshape, was developed in the high-temperature region with the use of memory functions (Ref. 3, Vol. 1).

In the present paper the method of memory functions is extended to the case of low temperatures. We note that we assume that the temperature of the Zeeman spin subsystem is low (the polarization of the nuclei is high, i.e., $\hbar\omega_0/kT \gtrsim 1$, where $\hbar\omega_0$ is the Zeeman splitting, k is Boltzmann's constant, and T is the absolute temperature), while the temperature of the secular dipole-dipole interactions is assumed to be high (spin-spin ordering is much smaller than the Zeeman ordering, i.e., $\hbar\omega_d \ll kT$, where $\hbar\omega_d$ is the average dipole-dipole interaction energy), which is entirely valid in the case of strong constant external magnetic fields (Ref. 3, Vol. 2).

2. LINESHAPE

As is well known, in the memory-function formalism the high-temperature theory of the shape of a resonance line consists of using the integrodifferential equation

$$\frac{dG_0(t)}{dt} = -\int_0^t K_0(t-t')G_0(t')dt', \qquad (1)$$

where $G_0(t)$ and $K_0(t)$ are, correspondingly, the high-temperature correlation functions of the lineshape and the memory, whose odd moments are equal to zero (Ref. 3, Vol. 1).

At low temperatures the situation is somewhat more complicated, since the odd moments of the low-temperature shape function $G(t)$ and memory function $K(t)$ are now different from zero [$K(t)$ is expressed in terms of the derivatives of the spin operators $I^{\pm}(t)$, from which the correlation function $G(t)$ is constructed[4,5]]. In what follows we take into account only the first N_1 and second N_2 moments of the memory function $K(t)$. It is easy to verify that for nonzero first moment M_1 of the function $G(t)$ the mathematical device employed in Ref. 3 (Vol. 1)—substitution of the Laplace transforms of the power series expansions of $G(t)$ and $K(t)$ into a Laplace transform equation of the type (1) for the functions $G(t)$ and $K(t)$—cannot be used to express the moments N_n of the memory function $K(t)$ directly in terms of the moments M_n of the correlation function of the lineshape $G(t)$ because the conditions for the applicability of the theorem concerning the convolution of functions in Laplace's method are not satisfied. For this reason, we employ at the outset the approximation[5]

$$G(t) = G_1(t)\exp(-iM_1t) \qquad (2)$$

and write an equation of the form (1) for the "unshifted" shape function $G_1(t)$:

$$\frac{dG_1(t)}{dt} = -\int_0^t K(t-t')G_1(t')dt', \qquad (3)$$

and in addition $K(0) = M_2'$ is the second moment of the function $G_1(t)$.

Applying to Eq. (3) the Laplace transform, we find

$$zG_1(z) - 1 = -K(z)G_1(z), \qquad (4)$$

whence we find

 0038-5646/92/040694-03$05.00

$$G_1(\Delta)=\pi^{-1}K'(\Delta)\{[K'(\Delta)]^2+[\Delta-K''(\Delta)]^2\}^{-1}, \quad (5)$$

where

$$\Delta=\omega-\omega_0=-iz, \quad K(i\Delta)=K'(\Delta)-iK''(\Delta), \quad (6)$$

and ω is the frequency of the alternating magnetic field.

As in Eq. (2), we separate from $K(t)$ the first moment N_1 and employ for the "unshifted" memory function $K_1(t)$ the usual Gaussian approximation

$$K(t)=K_1(t)\exp(-iN_1t)=M_2'\exp(-iN_1t-N_2't^2/2), \quad (7)$$

where M_2' and N_2' are the second moments of the functions $G_1(t)$ and $K_1(t)$, respectively, whose first moments are equal to zero ($M_1'=N_1'=0$). Laplace transforming Eq. (7) and using Eq. (6) we find

$$K_1'(\Delta)=\left(\frac{\pi}{2}\right)^{1/2}\frac{M_2'}{(N_2')^{1/2}}\exp\left[\frac{-(\Delta+N_1)^2}{2N_2'}\right], \quad (8)$$

$$K_1''(\Delta)=2^{1/2}\frac{M_2'}{(N_2')^{1/2}}D\left(\frac{\Delta+N_1}{(2N_2')^{1/2}}\right), \quad (9)$$

where

$$D(x)=\exp(-x^2)\int_0^x\exp(y^2)dy$$

is the Dawson (plasma dispersion) function, which has a bell-shape in the interval [0,0) with a maximum value of ≈ 0.54.[6]

We now express N_1 and N_2' in terms of the moments M_1, M_2, M_3, and M_4 of the shape function $G(t)$. For this we first find a relation between the moments of the functions $G_1(t)$, $K_1(t)$ and $G(t)$, $K(t)$. We differentiate the expression (2) with respect to time and find

$$M_1'=\frac{idG_1}{dt}\Big|_{t=0}=0, \quad M_2'=-\frac{d^2G_1}{dt^2}\Big|_{t=0}=M_2-M_1^2,$$
$$M_3'=\frac{-id^3G_1}{dt^3}\Big|_{t=0}=M_3+2M_1^3-3M_1M_2, \quad (10)$$
$$M_4'=\frac{d^4G_1}{dt^4}\Big|_{t=0}=M_4+6M_1^2M_2-4M_1M_3-3M_1^4.$$

Similarly, from Eq. (7) we obtain

$$N_2'=-\frac{d^2K_1}{dt^2}\Big|_{t=0}=N_2-N_1^2. \quad (11)$$

Substituting into Eq. (4) the expansions

$$G_1(z)=\frac{1}{z}\left(1-\frac{M_2'}{z^2}+\frac{iM_3'}{z^3}+\frac{M_4'}{z^4}+\ldots\right), \quad (12)$$

$$K(z)=\frac{M_2'}{z}\left(1-\frac{iN_1}{z}-\frac{N_2}{z^2}+\frac{iN_3}{z^3}+\ldots\right) \quad (13)$$

and using Eqs. (10) and (11), we find

$$N_1=M_3'/M_2', \quad (14)$$

$$N_2'=M_2'(\mu'-1)-(M_3'/M_2')^2, \quad (15)$$

where $\mu'=M_4'/(M_2')^2$.

Using now the expressions (8) and (9), keeping in mind the expressions (10), (14), and (15) and using the fact that, according to Eq. (2), $G(\Delta)=G_1(\Delta+N_1)$, we finally obtain from Eq. (5)

$$G(x)=\pi^{-1}a\{a^2\exp[-(x-b)^2]$$
$$+[x(2N_2')^{1/2}-2\pi^{1/2}aD(x+b)]^2\exp(x+b)^2\}^{-1}, \quad (16)$$

where

$$x=(\Delta+M_1)/(2N_2')^{1/2},\quad a=(\pi/2)^{1/2}M_2'/(N_2')^{1/2},\quad b=N_1/(2N_2')^{1/2}.$$

The formula (16) gives an analytical expression for the shape of the magnetic-resonance line at low temperatures in the memory-function formalism, taking into account both the shift and deformation of the line, which are determined by the moments M_1 and M_3, respectively. We note that, having written an equation of the form (1) for the memory function itself, we can take into account the contribution of the higher-order odd moments.

3. COMPARISON WITH EXPERIMENT

The following relations (Ref. 3, Vol. 2) are valid for a spherical sample of CaF_2 with a simple cubic lattice, a system of nuclear spins with $I=1/2$, and orientation of the external constant magnetic field $H_0\|[100]$:

$$M_1=0,\quad M_2=M_2(0)(1-p^2),\quad M_3\approx-0{,}39[M_2(0)]^{3/2}p(1-p^2),$$
$$M_4\approx2{,}18[M_2(0)]^2(1-p^2)(1-0{,}42p^2), \quad (17)$$

where p is the spin polarization and $M_2(0)$ is the second moment at high temperature ($p\ll1$). Substituting these expressions into Eqs. (10), (14), and (15) we obtain from Eq. (16).

$$f(x)=a_1\{a_1^2\exp[-(x-b_1)^2]$$
$$+[x(2(2{,}18-p^2))^{1/2}-\pi^{1/2}D(x-b_1)]^2\exp[(x-b_1)^2]\}^{-1}, \quad (18)$$

where

$$f(x)=\pi G(x)[M_2(0)]^{1/2},\quad a_1=\left(\frac{\pi}{2}\right)^{1/2}\frac{1-p^2}{(2{,}18-p^2)^{1/2}},$$
$$b_1=\frac{0{,}39p}{(2{,}18-p^2)^{1/2}}.$$

One can see that as $p\to0$ (high temperatures) $f(x)$ transforms into its high-temperature analog given in the monograph Ref. 3 (Vol. 1). The computer calculations, performed using the formula (18) for polarization $p_1=0.355$, $p_2=0.57$, $p_3=0.785$, and $p_4=0.87$, corresponding to the experimental values of Ref. 3 (Vol. 2), are presented in Fig. 1 (solid lines). In the same figure the dashed lines show the experimental curves of the absorption line shape for the same values of the polarizations (Ref. 3, Vol. 2).

Since for $M_1=0$ we have $M_4'/(M_2')^2=M_4/M_2^2$, it is easy to see that as $p\to0$ the function $f(x)$ assumes a shape close to Gaussian (for example, for $p=0.355$ we obtain $M_4/M_2^2\approx2.34$), while for $p\approx1$ the shape of the resonance curve is close to Lorentzian (for $p=0.87$ we have $M_4/M_2^2\approx5.36$), to which the resonance curves in the figure correspond. As for the ratios of the heights of the absorption lines, they are practically of the same order of magnitude as the experimental ratios [the height of the resonance line is mainly determined by the first term of the denominator in the formula (18)]. In the experiment, however, as one can see from the figure, the height of the line increases more rapidly with increasing polarization p than follows from the expression (18). For example, the ratio of the heights of the experimental lines, corresponding to the polarizations 0.87 and

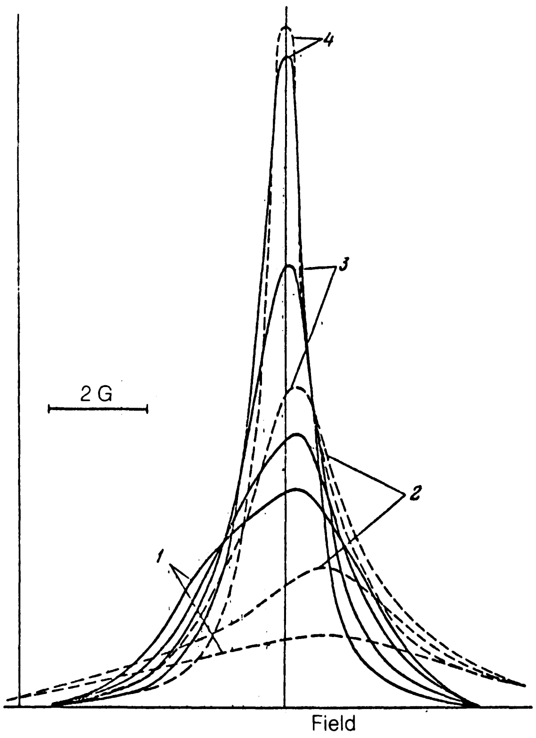

FIG. 1. Shape of the absorption signal for different values of the polarization: $p = 35.5\%$ (1), 57% (2), 78.5% (3), and 87% (4). The solid curves represent the calculation using the formula (18); the dashed curves represent the experimental results (Ref. 3, Vol. 2).

0.785, is equal to ≈ 2.3, while according to the formula (18) we have ≈ 1.48. The greatest difference occurs between the ratios of the heights of the absorption curves for the polarizations 0.87 and 0.355: ≈ 11.2 in the experiment and ≈ 3 from the expression (18).

The computational results also differ from the experiment in the base of the lines (on the wings of the resonance lines). This difference results from the fact that the present approximation takes into account only the second and fourth moments M_2 and M_4 of the lineshape. As one can see from the figure, the lineshape and linewidth agrees best with experiment in the case of highest polarization. It is obvious that the maxima of the experimental curves are shifted more for lower values of the polarizations, while for a polarization of $p = 87\%$ the shift of the top of the theoretical curve is insignificant. This can be explained by the fact that, first, in the present approximation, together with the higher order even moments of the lineshape ($M_6, M_8, \ldots$), the contributions of the higher odd moments ($M_5, M_7, \ldots$) are neglected and, second, according to Eq. (17), as $p \to 1$ the moment $M_3 \to 0$ and its contribution to the deformation of the line is minimal.

Finally, we note that the center of gravity of the curve is virtually unshifted because $M_1 = 0$; as one can see from Fig. 1, this also agrees with experiment.

We thank the participants of the Moscow seminar on magnetic resonance at the Institute of Radio Electronics of the Academy of Sciences of the USSR for helpful remarks. One of us (É. Kh. Kh.) thanks M. Chkhartishvili and L. Gobadze for assistance with the computer calculations.

[1)]Institute of Physics of the Republic of Georgia
[2)]Georgian Technical University

[1]S. M. Al'tshuler and B. M. Kozyrev, *Electron Paramagnetic Resonance of Compounds of Intermediate Group Elements* [in Russian], Nauka, Moscow, 1972.
[2]A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, Clarendon, Oxford, 1970, Vol. 1.
[3]A. Abragam and M. Goldman, *Nuclear Magnetism: Order and Disorder*, Clarendon, Oxford, 1982, Vols. 1 and 2.
[4]D. N. Zubarev, in *Itogi nauki i tekhniki. Sovremennye problemy matematiki* (*Progress in Science and Technology. Current Problems in Mathematics*) [in Russian], VINITI, Moscow, 1980, Vol. 15, p. 131.
[5]L. L. Buishvili and É. Kh. Khalvashi, *Radio Spectroscopy* [in Russian], Perm State University, Perm, 1987, p. 58.
[6]U. Gauchi, *Handbook of Special Functions* [in Russian], Nauka, Moscow, 1979, p. 119.

Translated by M. E. Alferieff