Bloch equations in the memory-function formalism

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(Submitted 6 February 1986)
Zh. Eksp. Teor. Fiz. **91**, 310–313 (July 1986)

The effect of saturation on the half-width δ of the magnetic-resonance absorption line is investigated using the Bloch equations with memory as a model. The relation $\delta \propto (\ln S)^{1/2}$ is deduced and indicates that there is practically no saturation broadening in this model.

1. INTRODUCTION

Bloch's equations for the magnetization components $M_{x,y,z}(t)$ are known not to hold for solids.[1,2] The resonance-line shape is therefore usually investigated by using the fluctuation-dissipation theorem[3] and is expressed in terms of the Fourier transform of the correlation function

$$G(t)=\mathrm{Sp}\,\{I_x I_x(t)\}/\mathrm{Sp}\, I_x^2,$$

where I_x is the total spin operator and the time dependence is determined by the broadening interaction $\mathscr{H}_{\rm sec}$. Since the function $G(t)$ cannot be rigorously calculated, the method of moments[4] is used, and $G(t)$ is approximated by a Lorentzian or a Gaussian profile[1], depending on the value of the parameter $\mu = M_4/M_2^2$ (M_2 and M_4 are the second and fourth moments of the resonance line). In the Gaussian case $\mu = 3$ and the line HWHM δ is determined only by the value of M_2. Actually, however, while the line shape in solids is close to Gaussian, nonetheless $\mu \neq 3$, and depends naturally also on the higher moments $M_4, M_6, \ldots$.

Substantial progress was made recently[5,6] towards more accurate calculation of δ. In particular, an integro-differential equation was derived that describes the spin-spin relaxation of the transverse magnetization components

$$\frac{dM_\alpha(t)}{dt}=-\int_0^t K(t-t')M_\alpha(t')\,dt', \qquad \alpha=x,y, \tag{1}$$

where $K(t-t')$ is the memory function. An explicit form of $K(t)$ is given in Refs. 5–7. Since $M_\alpha(t) \propto G(t)$, an identical equation holds also for the correlation function $G(t)$ itself.

The presence of memory in (1) is an indication that the total-spin operators $I_{x,y}$ do not commute with $\mathscr{H}_{\rm sec}$ and are therefore not quasi-integrals of the motion, so that the transverse components $M_{x,y}(t)$, like $G(t)$ and $K(t)$, vary rapidly, with a characteristic time $T_2 \sim \delta^{-1}$.

Equation (1) was used to calculate δ and to obtain expressions for the absorption and dispersion line shapes in the case of a weak alternating field.[5,6] In contrast to the method of moments mentioned above, the half-width δ contained M_4 and the line shape described the experimental data better.

Our aim was to investigate the effect of saturation on the resonance line width in the model of Bloch equations with memory.

2. BLOCH EQUATIONS WITH MEMORY

Consider the dynamics of a spin system in a magnetic field

$$\mathbf{H}(t)=H_0\mathbf{k}+H_1(\mathbf{i}\cos\omega t-\mathbf{j}\sin\omega t),$$

which is the sum of a constant field $\mathbf{H}_0 \| \mathbf{z}$ and a circularly polarized field of amplitude H_1 and frequency ω ($\mathbf{i}$, $\mathbf{j}$, and $\mathbf{k}$ are unit vectors along the axes x, y and z).

Replacing the relaxation term in the phenomenological Bloch equations[1] by integrals of the form (1), we obtain, in a coordinate frame rotating about the z axis at the Zeeman frequency $\omega_0 \approx \gamma H_0$, the equations

$$\begin{gathered}\frac{dM^\pm(t)}{dt}=\pm i\omega_1 M_z(t)e^{\mp i\Delta t}-\int_0^t K(t-t')M^\pm(t')\,dt',\\ \frac{dM_z(t)}{dt}=\frac{i\omega_1}{2}[M^+(t)e^{i\Delta t}-M^-(t)e^{-i\Delta t}]-\frac{M_z(t)-M_0}{T_1},\end{gathered} \tag{2}$$

where

$$M^\pm=M_x\pm iM_y, \quad \Delta=\omega-\omega_0, \quad \omega_1=\gamma H_1,$$

T_1 is the spin-lattice relaxation time, and M_0 is the equilibrium relaxation. When so generalized, Bloch's equations become suitable for the description of spin dynamics in solids for arbitrary interactions between the spins, and permit also a study of the influence of the saturation effects on the shape and width of the resonance line in the memory-function formalism. Note that Eqs. (2) can be easily derived by choosing $\hat{M}_{x,y,z}$ as the operators of interest and by using the method of Refs. 5 and 6. Making the change of variables $\widetilde{M}^\pm(t) = M^\pm(t)\exp(\pm i\Delta t)$, we obtain ultimately

$$\begin{gathered}\frac{d\widetilde{M}^\pm(t)}{dt}=\pm i\Delta\widetilde{M}^\pm(t)\pm i\omega_1 M_z(t)\\ -\int_0^t K(t-t')\exp[\pm i\Delta(t-t')]\widetilde{M}^\pm(t')\,dt',\\ \frac{dM_z(t)}{dt}=\frac{i\omega_1}{2}[\widetilde{M}^+(t)-\widetilde{M}^-(t)]-\frac{M_z(t)-M_0}{T_1}.\end{gathered} \tag{3}$$

Taking the Laplace transform of (3) (Ref. 8), in analogy with the procedure used in Ref. 6, we readily obtain a system of algebraic equations whose solution yields, for the initial conditions $M_z(0) = M_0$ and $\widetilde{M}^\pm(0) = M^\pm(0) = 0$,

$$\begin{gathered}\widetilde{M}^\pm(p)=\pm(M_0/pD)(p+1/T_1)i\omega_1[p+i\Delta+K(p+i\Delta)],\\ M_z(p)=(M_0/pD)(p+1/T_1)[p-i\Delta+K(p-i\Delta)]\\ \times[p+i\Delta+K(p+i\Delta)],\end{gathered} \tag{4}$$

 0038-5646/86/070181-02$04.00

where

$$D=(p+1/T_1)[p-i\Delta+K(p-i\Delta)][p+i\Delta+K(p+i\Delta)]+{}^1/_2\omega_1^2[2p+K(p-i\Delta)+K(p+i\Delta)]$$

and p is the variable of the Laplace transformation.

3. STATIONARY SOLUTION

To resolve Eqs. (4) into partial fractions and to take the inverse Laplace transforms, i.e., to obtain a general solution of Bloch's equation with memory, we need the explicit form of the memory function $K(t)$. Since however, the denominators of (4) have a root $p=0$, one of the partial fractions can be easily determined and yields a stationary solution of the system (3) without the use of the explicit form of $K(t)$. Omitting the straightforward calculations (the result is obtained by leaving out the p^{-1} term and then setting $p=0$), we give only the value of $\tilde{M}_{st}^+$, which determines the stationary process of absorption and dispersion of the alternating-field energy by the system of interacting spins, with account taken of the memory effects:

$$\tilde{M}_{st}^+=i\omega_1M_0[K(i\Delta)+i\Delta]\{[K(-i\Delta)-i\Delta][K(i\Delta)+i\Delta]+{}^1/_2\omega_1^2T_1[K(i\Delta)+K(-i\Delta)]\}^{-1}. \tag{5}$$

Since $K^*(t)=K(t)$ (the asterisk denotes complex conjugation), we get $K^*(i\Delta)=K(-i\Delta)$. Putting $K(\pm i\Delta)=K'(\Delta)\mp iK''(\Delta)$ and separating the real and imaginary parts of M_{st}^+, we get ultimately

$$\tilde{M}_{st}^+=i\pi\omega_1M_0[g_H(\Delta)+ig_H'(\Delta)], \tag{6}$$

where the functions

$$g_H(\Delta)=K'(\Delta)/\pi\{K'^2(\Delta)+[\Delta-K''(\Delta)]^2+\omega_1^2T_1K'(\Delta)\}, \tag{7}$$

$$g_H'(\Delta)=[\Delta-K''(\Delta)]/\pi\{K'^2(\Delta)+[\Delta-K''(\Delta)]^2+\omega_1^2T_1K'(\Delta)\} \tag{8}$$

are the waveforms of the absorption and dispersion signals with allowance for saturation.

In the presence of saturation, Eq. (6) coincides with Eq. (1.123) of the book of Abragam and Goldman.[6]

4. LINEWIDTH CALCULATION

We obtain an explicit expression for the half-width δ at half-maximum of the absorption line, using the Gaussian approximation of the memory function,[6] when

$$K'(\Delta)=\left[\frac{\pi M_2}{2(\mu-1)}\right]^{1/2}e^{-x^2},\quad K''(\Delta)=\left(\frac{2M_2}{\mu-1}\right)^{1/2}\Psi(x),$$

$$\Psi(x)=e^{-x^2}\int_0^x e^{y^2}dy, \tag{9}$$

where $x\equiv\delta(2N_2)^{-1/2}$, $N_2=M_2(\mu-1)$ is the second moment of the memory function, and $\Psi(x)$ is a special function expressed in terms of the error function of imaginary argument, with $|\Psi|_{\max}\approx0.5$ (Ref. 9).[1)] Putting $g_H(\delta)=(1/2)g_H(0)$, we get

$$\delta=K'(0)\left[\frac{K''(\delta)}{K'(0)}+\left[(2+s)\frac{K'(\delta)}{K'(0)}-\frac{K'^2(\delta)}{K'^2(0)}\right]^{1/2}\right\},$$
$$s=\pi g(0)\omega_1^2T_1=\omega_1^2T_1/K'(0), \tag{10}$$

where s is the saturation parameter and $g(0)=[\pi K'(0)]^{-1}$ is the maximum of the unsaturated line contour $g(\Delta)=g_H(\Delta)|_{\omega_1=0}$. Substituting (9) in (10) we get

$$\delta=\left[\frac{\pi M_2}{2(\mu_1-1)}\right]^{1/2}f_H(x,s),$$
$$f_H(x,s)=f(x)+e^{-x^2/2}[(2-e^{-x^2}+s)^{1/2}-(2-e^{-x^2})^{1/2}],$$
$$f(x)=(2-e^{-x^2})^{1/2}e^{-x^2/2}+2\pi^{-1/2}\Psi(x). \tag{11}$$

In the limit $s=0$ (zero saturation) expressions (11) go over into results of the theory expounded in Refs. 5 and 6.

5. CONCLUSION

We now investigate how δ depends on s and μ. Since $f(x)\approx1$ (Ref. 6), we get at saturation ($s\gg1$, $s^{1/2}\exp(-x^2)\gg1$)

$$\delta\approx\delta_0s^{1/2}\exp(-x^2/2),\qquad \delta_0\approx[\pi M_2/2(\mu-1)]^{1/2}, \tag{12}$$

where δ_0 is the unsaturated half-width. It follows from (12) that the dependence of s on x^2 is mainly exponential ($s\sim x^2\exp(-x^2)$), so that the inverse dependence of δ on s is very weak, i.e.,

$$\delta\approx2\delta_0(\mu-1)[(\ln s)/\pi]^{1/2}, \tag{13}$$

whereas the usual Block equations give rise to the stronger dependence $\delta\approx s^{1/2}\delta_0$. The $\delta\propto(\ln s)^{1/2}$ dependence is difficult to observe in experiment, thus attesting to practically no broadening by saturation in the model considered. That δ depends on s was observed earlier in experiments on magnetic-resonance saturation in solids,[10] and was explained by resorting to Provotorov's two-temperature theory.[11] It follows from this that an alternate explanation of the absence of broadening by saturation can be based on Bloch's equations with memory.

Comparison of δ with δ_0 shows that under saturation conditions the form of δ as a function of the parameter μ also changes, the more so the larger μ. We note also that account can be taken in the calculation of δ also of the contributions of the moments of higher order, M_6, M_8..., by writing an integrodifferential equation such as (1) for the memory function itself.[5,6]

[1)] We have used the representation $\exp(-x^2)F(1/2;3/2;x^2)=\Psi(x)/x$, where F is a confluent hypergeometric function.

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Translated by J. G. Adashko