

Low-frequency paramagnetic susceptibility under conditions of shift of the spin-spin temperature

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Expressions for the low-frequency paramagnetic susceptibility $\chi(\omega)$ measured in parallel fields are obtained on the basis of the Provotorov equations under conditions of a shift of the spin-spin temperature T_{SS} due to saturation of paramagnetic resonance and to cross relaxation. It is shown that such a shift of T_{SS} may lead to enhancement of the absorption and dispersion signals (χ'' and χ') by approximately T_0/T_{SS} times (T_0 is the lattice temperature). This is an increase by two or three orders of magnitude. In effect the phenomenon may be regarded as a transfer of the paramagnetic resonance signal to low frequencies. Its application should sharply raise the sensitivity of the conventional parallel-field method.

1. INTRODUCTION AND FORMULATION OF PROBLEM

Back in the thirties, long before the discovery of paramagnetic resonance, a method was developed for the investigation of parametric relaxation. This method is based on measuring the paramagnetic susceptibility $\chi(\omega)$ at relatively low frequencies (up to $10^6 = 10^7$ Hz). This procedure, frequently called the "parallel-field method" (the alternating magnetic field is parallel to the constant field during the measurements), was initiated by Dutch physicists, especially by Gorter's group^[1]. The "Dutch" method was regarded in its time as quite fruitful; thus, it was used to observe for the first time and to study spin-lattice and spin-spin relaxation process. However, following the discovery^[2] and rapid development of the paramagnetic-resonance method, which is much more sensitive, the low-frequency procedure was pushed into the background and apparently is used at present in only two or three laboratories. One of them is the original laboratory in Leiden (see, for example, ^[3]).

This article deals with the application of the low-frequency "parallel field" method under conditions of simultaneous saturation of paramagnetic resonance by a high-frequency field. As will be shown below, appreciable enhancement of the low-frequency absorption and dispersion signals should be produced in this case by the strong change in the temperature of the spin-spin interactions of the solid paramagnets. This means, in particular, a sharp increase (by 2 or 3 orders of magnitude) in the sensitivity of the measurement in "parallel fields," giving grounds for hope of a revival of interest in this method as an effective tool for the investigation of paramagnetic crystals.

In the classical variant of the "Dutch" method, an alternating magnetic field $H_1 e^{i\omega t}$ is applied to a paramagnetic sample placed in a constant magnetic field H_0 parallel to the alternating field ($H_1 \ll H_0$), and the susceptibility $\chi(\omega) = \partial M_Z / \partial H$ at the frequency ω is measured (M_Z is the projection of the macroscopic magnetic moment of the sample on H_0). If the longitudinal relaxation of the magnetic moment is described by very simple equations of the type

$$\partial M_z / \partial t = -\tau_1^{-1} (M_z - M_{z0}), \quad (1)$$

where M_{z0} is the equilibrium value of M_Z and τ_1 is the time of the spin-lattice relaxation, then the modula-

tion of the external magnetic field, described by the law $H = H_0 + H_1 e^{i\omega t}$, leads to a corresponding synchronous modulation of the calculated value of M_{z0} , namely $M_{z0}(t) = \chi_0 (H_0 + H_1 e^{i\omega t})$, where χ_0 is the static susceptibility. The true value of $M_Z(t)$ will obviously also be modulated with frequency ω , but will lag $H(t)$ and $M_{z0}(t)$ in phase; it is the depth and phase of this modulation that determine the sought value of $\chi(\omega)$, viz., $M_Z(t) = \chi_0 H_0 + \chi(\omega) H_1 e^{i\omega t}$. Substituting $M_{z0}(t)$ and $M_Z(t)$ in (1), we obtain the well-known expression^[1]

$$\chi(\omega) = \chi_0 / (1 + i\omega\tau_1). \quad (2)$$

(We neglect here the "adiabatic" susceptibility, which is due to the direct thermal mixing of the Zeeman energy with the spin-spin interaction energy^[1,4], and plays an inessential role in strong magnetic fields. It will be shown below that this susceptibility cannot be neglected under resonance saturation conditions.)

It is easy to obtain from (2) the real and imaginary parts of $\chi(\omega)$, denoted by $\chi'(\omega)$ and $-\chi''(\omega)$, respectively, and proportional to the dispersion and absorption signals. It is obvious that, for example, the maximum of $\chi''(\omega)$ is reached at $\omega = \tau_1^{-1}$ and is equal to $\chi_0/2$. The derivation of the expressions for $\chi(\omega)$ in the presence of other relaxation processes, for example cross relaxation, is similar^[5].

We assume now that the sample is acted upon, in addition to the field $H_1 e^{i\omega t}$, by a high-frequency magnetic field $h_1 e^{2\pi i \nu t}$ perpendicular to H_0 and saturating the paramagnetic resonance at a frequency ν close to the central frequency ν_0 of the resonance line. Let the line broadening be homogeneous and be determined by the spin-spin interaction of like spins.

As is well known^[6-8] at $\nu \neq \nu_0$ such a saturation causes a strong shift of the temperature of the spin-spin interactions, as a result of which the difference of the populations at the Zeeman levels of the spin system does not vanish. The "residual" population difference, and correspondingly the nonzero z-component of the magnetic moment (directed along the "effective field" in a coordinate system that rotates with the frequency ν ^[6]), depend strongly on the detuning $\Delta = \nu - \nu_0$.

Thus, for example, a change of H by an amount equal to the line width δH , leading to a shift of the saturation point from the remote wing of the line to its center, causes a decrease of M_Z from a value close to M_{z0} to

zero. This means that the corresponding susceptibility is of the order of

$$|\chi| \approx \left| \frac{\Delta M_z}{\Delta H} \right| \approx \frac{M_{z0}}{\delta H} = \chi_0 \frac{H_0}{\delta H} \sim (10^3 - 10^4) \chi_0.$$

Thus, a not-strictly-resonant saturation of the line causes $|\chi|$ to increase 2–3 order of magnitude.

For a more accurate determination of $\chi(\omega)$ we use the Provotorov equations^[7], which describe the saturation of the spin system in a solid:

$$\begin{aligned} \frac{\partial}{\partial t} \alpha &= -w(\alpha + \gamma\Delta) - \frac{1}{\tau_1}(\alpha - \alpha_0), \\ \frac{\partial}{\partial t} (\gamma\Delta) &= -\frac{\Delta^2}{\nu_L^2} w(\alpha + \gamma\Delta) - \frac{1}{\tau_1'}(\gamma\Delta - \gamma_0\Delta), \end{aligned} \quad (3)$$

where $\alpha = h\nu_0/kT_Z$, $\gamma = h/kT_{SS}$, w is the probability of the stimulated transition at the frequency ν , ν_L^2 is the mean-squared "local field" due to the spin-spin interactions (in frequency units), τ_1 is the spin-lattice relaxation time of the spin-spin-interaction reservoir ("SS reservoir"), T_Z and T_{SS} are the spin temperatures of the Zeeman and SS reservoirs, and α_0 and γ_0 are the equilibrium values of α and γ at the lattice temperature T_0 .

When the susceptibility is measured at the frequency ω , the magnetic-field modulation becomes manifest in a corresponding synchronous modulation of the detuning: $\Delta = \Delta_0 + \Delta_1 e^{i\omega t}$. For a simple two-level system we have $h\nu_0 = g\beta H$ (β is the Bohr magneton), so that $\partial/\partial H = -(g\beta/h)\partial/\partial \Delta$. Recognizing that $M_Z = (\frac{1}{2})N\alpha g\beta S$ (N is the number of spins per unit volume), we obtain

$$\chi = \frac{\partial M_z}{\partial H} = -\frac{g^2\beta^2}{2h} NS \frac{\partial \alpha}{\partial \Delta}. \quad (4)$$

We consider below only the case of sufficiently strong saturation, $w \gg \tau_1^{-1}(T_1')^{-1}$ (but under the condition $g\beta h_1 \ll h\nu_L$, which must be satisfied if the equations in (3) are to hold), and assume also that the amplitude H_1 of the modulation of the parallel field is small enough to be able to neglect its influence on the spin temperatures averaged over the period $2\pi/\omega$, i.e., we disregard the "modulation saturation" (see, for example,^[9,10]).

2. ADIABATIC SUSCEPTIBILITY

We consider first a case when the frequency ω is high enough to be able to neglect the spin-lattice relaxation in the measurement of $\chi(\omega)$, i.e., $\omega \gg \tau_1^{-1}$, $(\tau_1')^{-1}$. From Eq. (3), in which it is now necessary to omit the lattice terms, we can obtain

$$\frac{\partial}{\partial t} \alpha = -\frac{1}{\tau_1}(\alpha - \alpha_{ad}), \quad (5)$$

where τ_S is the time for establishment of saturation (it is also the time necessary for a single temperature to become established in the rotating coordinate frame^[6]), $\tau_S^{-1} = (1 + \Delta^2/\nu_L^2)w$, and α_{ad} is the calculated "adiabatic" value of α to which the true value $\alpha(t)$ tends in the saturation process. Since α_{ad} corresponds to the state of completed saturation, it satisfies the condition^[7]

$$\alpha + \gamma\Delta = 0. \quad (6)$$

The value of α_{ad} at specified initial conditions is a unique function of Δ (see formulas (11) and (12) below), and its harmonic part, of course, varies in phase with $\Delta(t)$, whereas the oscillating part of $\alpha(t)$ lags in phase, since $\tau_S \neq 0$.

Using (4), we can easily obtain from (5), in analogy with (1) and (2), the value of the susceptibility under saturation conditions:

$$\chi_s = \chi_{ad} / (1 + i\omega\tau_s), \quad (7)$$

where

$$\chi_{ad} = \frac{1}{2} N g \beta S \delta \alpha_{ad} / \partial H. \quad (8)$$

To find $\partial\alpha_{ad}/\partial H = -(g\beta/h)\partial\alpha_{ad}/\partial\Delta$, we note that the change of Δ under saturation conditions, when insulated from the lattice, is thermodynamically an adiabatic (isentropic) process. The entropy conservation condition then takes the form (see, for example,^[10])

$$\frac{\partial}{\partial \Delta} \left[\text{const} \cdot \alpha_{ad}^2 \left(1 + \frac{\nu_L^2}{\Delta^2} \right) \right] = 0,$$

From which we obtain, taking (6) into account,

$$\frac{\partial \alpha_{ad}}{\partial \Delta} \approx -\gamma_{ad}^0 \frac{\nu_L^2}{(\Delta_0^2 + \nu_L^2)}. \quad (9)$$

We have neglected in (9) the oscillating parts of the quantities γ_{ad} and Δ in comparison with the dc components γ_{ad}^0 and Δ_0 (corresponding to $t = 0$, $2\pi/\omega, \dots$). From (8) and (9) we get

$$\chi_{ad} = \chi_0 \frac{T_0}{T_{SS}^0} \frac{\nu_L^2}{(\Delta_0^2 + \nu_L^2)}, \quad (10)$$

where the static susceptibility is

$$\chi_0 = N g^2 \beta^2 S / 2kT_0,$$

and the value of $T_{SS}^0 \equiv h/k\gamma^0$ is determined by the state of the system at the instant when the susceptibility is measured, and depends on the time t' elapsed after the saturating power is turned on. If the measurement is performed after the completion of the saturation but before the influence of the lattice comes into play, i.e., at $\tau_S \ll t' \ll \tau_1, \tau_1'$, then the quantity T_{SS}^0 will be given by the solution of (3) without the lattice terms with initial conditions $T_Z = T_{SS} = T_0$ ^[8,10]:

$$\frac{T_0}{T_{SS}} = -\frac{kT_0}{h\Delta} \alpha = -\frac{\nu_0}{\Delta} \left(1 + \frac{\nu_L^2}{\Delta^2} \right)^{-1} \quad (11)$$

(To find T_{SS}^0 it is necessary to put here and subsequently $\Delta = \Delta_0$).

In the more realistic case when the measurement is carried out at $t' \gg \tau_S, \tau_1, \tau_1'$, it is necessary to use for T_0/T_{SS}^0 the stationary solution of (3)^[8]:

$$\frac{T_0}{T_{SS}} = -\frac{kT_0}{h\Delta} \alpha^* = -\frac{\nu_0}{\Delta} \left(1 + \frac{a\nu_L^2}{\Delta^2} \right)^{-1}, \quad (12)$$

where $a = \tau_1/\tau_1'$.

It is obvious that in any case χ_{ad} exceeds χ_0 by an approximate factor $T_0/T_{SS}^0 \sim \nu_0/\nu_L$, thus confirming our preliminary estimate.

3. SUSCEPTIBILITY DUE TO SPIN-LATTICE RELAXATION

We now consider low frequencies, $\omega \ll \tau_S^{-1}$, and take the spin-lattice relaxation into account. We assume that the saturation condition (6) is now satisfied at each instant of time. Taking (6) into account, we obtain from (3)

$$\frac{\partial}{\partial t} \alpha = -\frac{1}{\tau_1^*}(\alpha - \alpha^*), \quad (13)$$

where $\tau_1^* = \tau_1(\Delta^2 + \nu_L^2)/(\Delta^2 + a\nu_L^2)$ is the so-called "spin-lattice relaxation time in the rotating coordinate system"^[8], and $\alpha^* \equiv \alpha^*(t)$ is the calculated value of α under stationary conditions of completed spin-lattice

relaxation. The quantity $\alpha^*(t)$ is determined from (12); it corresponds to the instantaneous value of $\Delta(t)$ and obviously oscillates in phase with Δ :

$$\alpha^*(t) = (\alpha^*)^0 + \frac{\partial \alpha^*}{\partial \Delta} \Delta_1 e^{i\omega t}. \quad (14)$$

Equation (13) describes only that part of the change of α which is due to its tending to the value α^* as a result of spin-lattice relaxation. To obtain the complete derivative $d\alpha/dt$ it is necessary to add to the right-hand side of (13) a term that takes into account the change of α considered in the preceding section, which does not depend on the spin-lattice relaxation (it corresponds to a susceptibility $\chi_S(\omega)$ that coincides with χ_{ad} at $\omega \ll \tau_S^{-1}$).

Thus

$$\frac{d\alpha}{dt} = \left(\frac{\partial \alpha}{\partial t} \right)_l + \left(\frac{\partial \alpha}{\partial t} \right)_{ad} = -\frac{1}{\tau_1} (\alpha - \alpha^*) + \left(\frac{\partial \alpha}{\partial t} \right)_{ad}, \quad (15)$$

with

$$\alpha(t) = \alpha^0 + \left(\frac{\partial \alpha}{\partial \Delta} \right)_l \Delta_1 e^{i\omega t} + \left(\frac{\partial \alpha}{\partial \Delta} \right)_{ad} \Delta_1 e^{i\omega t}, \quad (16)$$

where the subscripts l and ad denote respectively the variations of α as a result of the spin-lattice relaxation and the adiabatic change in the detuning Δ .

Substituting (14) and (16) in (15), we obtain, taking (4) into account

$$\chi(\omega) = \chi_l(\omega) + \chi_{ad} = \frac{\chi^* - \chi_{ad}}{1 + i\omega\tau_1} + \chi_{ad}, \quad (17)$$

where $\chi_l(\omega)$ is the susceptibility due to the spin-lattice relaxation, χ_{ad} is determined from (10), and χ^* is the "stationary" susceptibility corresponding to $\partial \alpha^*/\partial \Delta$. Determining the latter with the aid of (12) and again taking (4) into account, we obtain

$$\chi^* = 2\chi_0 \frac{T_0}{T_{SS}^0} \frac{a\nu_L^2}{(\Delta_0^2 + a\nu_L^2)}. \quad (18)$$

Thus, the ratio $|\chi_l/\chi_0|$ can also reach values on the order of $|T_0/T_{SS}^0|$.

Finally, combining the results of (7) and (17), we can write down an expression for $\chi(\omega)$ at an arbitrary frequency:

$$\chi(\omega) = \frac{\chi_0^* - \chi_{ad}}{1 + i\omega\tau_1} + \frac{\chi_{ad}}{1 + i\omega\tau_1}. \quad (19)$$

4. CROSS-RELAXATION SUSCEPTIBILITY

An additional contribution to $\chi(\omega)$ can be made by the cross relaxation process^[5]. Assume, for example, that the substance contains two types of spins with Larmor frequencies $\nu_1 = h^{-1}g_1\beta H$ and $\nu_2 = h^{-1}g_2\beta H$, with $\nu_2 \approx \nu_1$ and $\Delta_{21} \equiv \nu_2 - \nu_1 \neq 0$. Then each elementary act of cross relaxation, which consists of simultaneous flipping of the spins 1 and 2 in opposite directions, leads to a change in the summary value of M_Z by an amount $(\frac{1}{2})\beta |g_1 - g_2|$ (we assume that $S_1 = S_2 = \frac{1}{2}$).

If the cross relaxation is effective in comparison with the spin-lattice relaxation, i.e., if its probability $w_{cr} \gg \tau_1^{-1}$, $(\tau_1')^{-1}$, then the process will tend to establish a dynamic equilibrium characterized by the relation^[11]

$$(\alpha_1 - \alpha_2 + \gamma_{cr}) = 0 \quad (20)$$

(the subscripts 1 and 2 label throughout the corresponding spin subsystem, and γ_{cr} and $h\Delta_{21}/kT_{SS}$).

Since the condition (20) depends explicitly on the detuning Δ_{21} , any variation of the latter leads to a change

in the ratio of α_1 to α_2 , and consequently also to a change of M_Z , meaning the appearance of cross-relaxation susceptibility $\chi_{cr} = (\partial M_S / \partial H)_{cr}$.

To simplify the calculation of χ_{cr} , we consider only very rapid cross relaxation and sufficiently high frequencies:

$$w_{cr}, \omega \gg \tau_1^{-1}, (\tau_1')^{-1}.$$

In this case $\chi_l(\omega), \chi_S(\omega) \rightarrow 0$ and $\chi(\omega)$ is due only to the "pure" cross relaxation, while the roles of saturation and the lattice reduce only to specifying the dc components T_Z^0 and T_{SS}^0 (i.e., those averaged over the period) of the spin temperatures. (We note that a similar problem was considered in^[5], but the shift of the spin-spin temperatures, which is very important under resonance-saturation conditions, was not taken correctly into account.) To obtain the correct results, we start from the Provotorov cross-relaxation equations^[11], from which it is necessary to omit in this case the terms describing the saturation and the spin-lattice relaxation:

$$\begin{aligned} \frac{\partial}{\partial t} \alpha_1 &= \frac{N_2}{N} w_{cr} (\alpha_2 - \alpha_1 - \gamma_{cr} \Delta_{21}), \\ \frac{\partial}{\partial t} \alpha_2 &= -\frac{N_1}{N} w_{cr} (\alpha_2 - \alpha_1 - \gamma_{cr} \Delta_{21}), \\ \frac{\partial}{\partial t} (\gamma_{cr} \Delta_{21}) &= \frac{N_1 N_2}{N^2} \frac{\Delta_{21}^2}{\nu_L^2} w_{cr} (\alpha_2 - \alpha_1 - \gamma_{cr} \Delta_{21}), \end{aligned} \quad (21)$$

where $N = N_1 + N_2$.

Putting $N_1 N_2 / N^2 \equiv b$ and $\alpha_1 - \alpha_2 \equiv \alpha_{cr}$, we obtain from (21):

$$\begin{aligned} \frac{\partial}{\partial t} \alpha_{cr} &= -w_{cr} (\alpha_{cr} + \gamma_{cr} \Delta_{21}), \\ \frac{\partial}{\partial t} (\gamma_{cr} \Delta_{21}) &= -b \frac{\Delta_{21}^2}{\nu_L^2} w_{cr} (\alpha_{cr} + \gamma_{cr} \Delta_{21}). \end{aligned} \quad (22)$$

Equations (22) are analogous to (3) without the lattice terms, so that we can immediately write down for $\chi_{cr}(\omega)$ an expression analogous to (10), provided only we replace (4) by the relation

$$\chi_{cr} = \left(\frac{\partial M_z}{\partial H} \right)_{cr} = -\frac{N_1 N_2}{2N} \frac{\beta^2}{h} (g_2 - g_1)^2 S \frac{\partial \alpha_{cr}}{\partial \Delta_{21}} \quad (23)$$

(in the derivation of (23) we used the constancy of the sum $N_1 \alpha_1 + N_2 \alpha_2$ in the cross-relaxation process, see^[5]).

Taking (23) into account, we obtain

$$\begin{aligned} \chi_{cr}(\omega) &= (\chi_{cr})_{ad} / (1 + i\omega\tau_{cr}), \\ \tau_{cr}^{-1} &= w_{cr} (1 + b\Delta_{21}^2 / \nu_L^2), \end{aligned} \quad (24)$$

$$(\chi_{cr})_{ad} \approx \chi_0 \frac{T_0}{T_{SS}^0} \frac{(g_2 - g_1)^2}{\bar{g}^2} \frac{b\nu_L^2}{(b\Delta_{21}^2 + \nu_L^2)} \quad (25)$$

where $\bar{g} = (g_1 + g_2)/2$ and T_{SS}^0 is specified by the condition that one of the resonance lines be saturated and is determined by expressions similar to (11) and (12)^[8,12].

If we introduce the second moment $M_2 = b\Delta_{21}^2$ of the spin distribution over the frequencies ν_1 and ν_2 relative to the center of gravity of the spectrum, then expression (25) takes the form

$$(\chi_{cr})_{ad} = \chi_0 \frac{d}{dH} (\overline{M_2}) \frac{h^2}{\beta^2 \bar{g}^2} \frac{\nu_L^2}{(M_2 + \nu_L^2)} \frac{T_0}{T_{SS}^0}. \quad (26)$$

Starting from the existing analogy in the behavior of lines that are homogeneously broadened by spin-spin interactions, on the one hand, and inhomogeneous lines (or spectra) coupled by effective cross relaxation^[13], on the other, we can assume that formulas (24) and (26)

are approximately suitable also for the description of such "quasi-homogeneous" systems, where M_2 now denotes the second moment of the distribution of the spins over the "packets," and τ_{CR} is a certain averaged time of the cross relaxation between them.

5. DISCUSSION OF RESULTS

Figure 1 shows approximate plots of the real and imaginary parts of the total susceptibility, including (19) and (24) for the case $\tau_1^* > \tau_S > \tau_{CR}$. In addition to the information on the relaxation-process times usually obtained by the parallel-field method, plots of the type of Fig. 1 can yield information on the SS reservoir (for example, on the value of ν_L^2). Here the main difference from the usual "Dutch" method is the very large absolute values of the absorption and dispersion signals. Thus, for example, at a maximum stationary spin-spin temperature shift $|T_0/T_{SS}^*|_{\max} = \nu_0/2\sqrt{a\nu_L}$, which occurs when $\Delta_0 = \sqrt{a\nu_L}^{[8]}$ (see (12)), the maximum of χ_S'' (at $\omega = \tau_S^{-1}$), as seen from (10) and (18), amounts to $(\nu_0/8a^{3/2}\nu_L)\chi_0$. Thus, at $a = 2-3^{[6-14]}$ the effect is only slightly weaker than the resonant absorption, $\chi_{res}'' \sim \nu_{\chi_0}/\delta\nu$ ($\delta\nu$ is the half-width of the resonance line)^[15]. This enables us to speak of a shift, as it were, of the paramagnetic-resonance signal into the region of low frequencies.

The statements made above become particularly clear if we consider not the function $\chi(\omega)$ but the function $\chi(H_0)$ at $\omega = \text{const}$, as is usually done in magnetic-resonance spectroscopy. With the saturating signal permanently turned on at the frequency ν , slow passage of the field H_0 through the resonance region $H_0 \approx h\nu/g\beta$ leads to the appearance of absorption and dispersion signals at a fixed frequency ω (these signals are particularly strong at $\omega = (\tau_1^*)^{-1}, \tau_S^{-1}$, or τ_{CR}^{-1} , see Fig. 2). It is interesting that the $\chi''(H_0)$ curve, which is shown in the same figure, is antisymmetrical with respect to the point $\Delta_0 = 0$. In particular, at $H_0 < h\nu/g\beta$ (i.e., at $\Delta_0 > 0$), it follows from (12) that $T_0/T_{SS} < 0$, so that the absorption χ'' is negative, and energy is released at the frequency ω . (The negative susceptibility is due here to the fact that an increase of H_0 means an approach to the exact resonance and therefore causes a decrease of M_Z .)

Let us now estimate the numerical values of ω that are optimal for the observation of the effects. For EPR in dilute paramagnetic crystals at helium temperatures we have $\tau_1^* \sim \tau_1 \sim 10^{-1} - 10^{-4}$ sec, i.e., frequencies up to 10 kHz are needed to observe χ_1'' . The time τ_S can be much shorter, namely, $\tau_S^{-1} \sim \omega \sim (g\beta h_1)^2/h\delta\nu$ (we

note that the relaxation absorption signal χ_S'' , which has a maximum at $\omega = \tau_S^{-1}$, must not be confused with the resonant absorption in a rotating coordinate frame^[6], which occurs at a different frequency, $\omega/2\pi = g\beta h_1/h$). At $h_1 = 1$ Oe and $\delta\nu = 10$ Oe, we have $\tau_S^{-1} \sim 3 \times 10^6$ sec⁻¹, so that ω falls in the megacycle band. The quantity χ_{CR} can also be measured at higher frequencies.

For NMR, the optimal range of ω turns out to be at a much lower frequency, as a result of which the sensitivity of the measurements is low. Nonetheless, the large ratio ν_0/ν_L , which is characteristic of Gaussian NMR lines in solids, still gives grounds for hoping to observe the effects.

We note that application of an alternating field parallel to H_0 is not the only way of modulating M_Z under resonance-saturation conditions. There are also other suitable methods, for example frequency or amplitude modulation of the saturating signal, or else (for anisotropic paramagnets), modulation of the angle between H_0 and the magnetic axis of the crystal. (The last method can be realized, for example, by making the fields H_0 and $H_1 e^{i\omega t}$ perpendicular to each other.) In all these cases one should speak not of the susceptibility proper $\partial M_Z/\partial H$, but of a certain response of M_Z to a harmonic signal. One can investigate also the response of M_Z to a pulsed signal (for example, turning the saturation on or off); such a procedure^[16,17] obviously is connected with our procedure by a Fourier transformation.

Notice should also be taken of the possible appearance of signals of the type shown in Fig. 2, but not connected with a shift of the temperature T_{SS} . The reason may be simply the dependence of the saturation factor s (meaning also M_Z) on the detuning Δ , a dependence due to the shape of the resonance line. It is clear that this parasitic effect should vanish when the pump power is increased up to $s \gg 1$. A similar dependence of M_Z on Δ , which also produces a parasitic signal χ , can result also from "hole burning" on the wing of an essentially inhomogeneous line. These effects, which make the interpretation of the possible experiments somewhat more difficult, can, on the other hand, also be used to "transfer" the paramagnetic resonance to the low-frequency band.

We note, finally, that the nonlinear dependence of α on Δ (see (11), (12)) should lead to the appearance of an alternating magnetization with frequency 2ω . Although this effect has been ignored in the present paper, since we have been interested only in $\chi(\omega)$, it is apparently of independent interest.

In conclusion, the author is sincerely grateful to M. E. Zhabotinskiĭ for interest in the work and to M. I. Rodak for useful discussions and a number of valuable remarks.

Note added in proof (18 January 1973). The here-described enhancement of the parallel susceptibility was recently observed experimentally (V. A. Atsarkin and O. A. Ryabushkin, ZhETF Pis. Red. 17, 103 (1973) [JETP Lett. 17, 71 (1973)]).

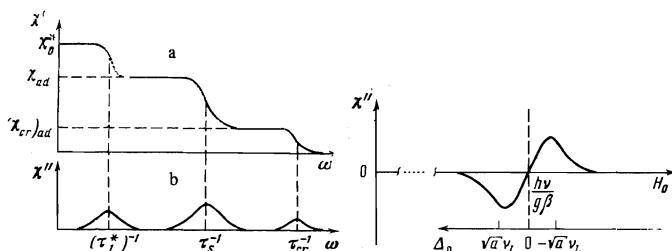


FIG. 1

FIG. 2

FIG. 1. Approximate plots of $\chi'(\omega)$ (a) and $\chi''(\omega)$ (b) under saturation and cross-relaxation conditions.

FIG. 2. Approximate plot of χ'' against H_0 in the region $H_0 \approx h\nu/g\beta$ (ν is the saturation frequency) at a fixed value of ω .

¹⁾Goldman ^[9] considers also the modulation of the external magnetic field under conditions of resonance saturation. His aim, however, is in essence the opposite of ours, since he calculates the influence of the field modulation on the resonant absorption and dispersion signals

registered at a frequency ν , whereas we seek to determine the influence of the resonant saturation on the signal $\chi'(\omega)$ and $\chi''(\omega)$, which are registered in the modulation circuit itself.

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