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Dispersion, a Most Useful Tool in Paramagnetic Resonance

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The authors present a theoretical and experimental study on the possibilities of paramagnetic-resonance dispersion for investigating the properties of paramagnetic systems. It is shown that the dispersion line contains at least as much (and "better") information about the magnetic relaxation as does the absorption line. The parameters of both resonance lines and their relation to parameters of the relaxation function are discussed. New parameters of the dispersion line are introduced, corresponding and equivalent to the area under and the moments of the absorption line. These dispersion parameters are related to the static susceptibility and the derivatives of the relaxation function in a much simpler way than the corresponding absorption parameters. The foregoing results, being derived essentially for the ideal case of a symmetric nonsaturated line in a high magnetic field, are generalized afterwards to some nonideal cases. Experimental methods, applying the theoretical principles introduced in the paper are described, amongst others a simple, accurate, and selective method for measuring the static susceptibility by means of resonance dispersion. In order to check those experimental principles, a series of test measurements of the static susceptibility of diphenylpicrylhydrazyl (DPPH) were performed in a 9-GHz ESR spectrometer. An excellent reproducibility was found, without using any reference substance, and even after complete deregulation of the spectrometer. Low-temperature measurements were included. The values of the static susceptibility found by the resonance-dispersion method are compared with those of other authors, obtained by means of static methods. The Curie temperatures are calculated and some deviations from the Curie-Weiss law are discussed. A possible influence of the air surrounding some of the samples is detected.

INTRODUCTION

IN almost all paramagnetic-resonance studies, absorption rather than dispersion is used, except in the case of appreciable saturation, where the absorption is too weak. In the present paper we want to demonstrate that it is quite interesting, even in the case of negligible saturation, to make use of resonance dispersion for studying paramagnetic systems.

In interpreting magnetic-resonance experiments, scholars almost exclusively use the *relaxation function*, to which the absorption line is related by the g factor, the linewidth, the area under the curve, and the moments of the line.

In the first section of this paper we will show that the dispersion line contains at least the same—and even "better"—information about the relaxation function as the absorption line. For clarity we will restrict ourselves in this section to the discussion of a simple symmetric line in a high static field. The conclusions will then be generalized to some extent in the second section. In the third section it will be emphasized that, from an experimental point of view, information on the relaxation function should be more accessible in the dispersion line, and that resonance dispersion really is a useful and practical tool for the investigation of magnetic properties. The fourth section contains direct experimental evidence on this question.

I. DISPERSION, ABSORPTION, AND RELAXATION

A. Transformation of the Relaxation Function—Quantities of Interest

The relation existing between relaxation and high-frequency (HF) susceptibility, and more generally between transient and steady-state response of a system, constitutes precisely the physical background of the well-known Fourier transformation.

Let $m(t)$ be the magnetization following a unit step function of magnetic field b, ending at time $t=0$. The resulting *complex susceptibility* is then given by

$$\chi(\omega)\equiv\chi'-i\chi''=\int_0^\infty(-dm(t)/dt)\exp(-i\omega t)dt.$$

On physical grounds we assume $\chi(\infty)$ to be zero.[1] In the presence of a static magnetic field B_s, the function $m(t)$ undergoes an oscillation at a certain frequency ω_s, and $\chi(\omega)$ becomes important in the neighborhood of that *resonance frequency*.

In the present section we suppose B_s constant, while ω is variable, and we confine ourselves to the case of one single resonance frequency, which we assume to be much higher than $1/\tau$, where τ is the characteristic time of $m(t)$ if one disregards oscillations. The frequency range where $\chi(\omega)$ is enhanced is of the order of $1/\tau$, and pretty well centered on $\omega_s=-\gamma B_s$, where γ is the gyromagnetic ratio.

By introducing a new quasi-step-function for the

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[1] C. P. Slichter, *Principles of Magnetic Resonance* (Harper and Row, New York, 1964), p. 36.

magnetic pulse:

$$b_1 = \cos\omega_s t \quad \text{for} \quad t<0,$$
$$b_1 = 0 \quad \text{for} \quad t \geqslant 0,$$

we may write the response magnetization as

$$m_1(t) = \psi(t)\cos\omega_s t,$$

which relation defines the so-called *transformed* relaxation function $\psi(t)$. In the limit $\tau \gg 1/\omega_s$, considered here, $m(t) = m_1(t)$. Further we define

$$\omega_d \equiv \omega - \omega_s,$$

and confine ourselves to symmetric lines, i.e., lines satisfying the following condition:

$$\chi(\omega_d) = -\chi^*(-\omega_d).$$

With some mathematics, carried out more extensively elsewhere,[2,3] and disregarding the line centered on $\omega = -\omega_s$, we arrive at the following inverse Fourier transforms:

$$\psi(t) = (2/\pi\omega_s)\int_{-\infty}^{+\infty} -\chi' \sin\omega_d t \, d\omega_d, \tag{1a}$$

$$\psi(t) = (2/\pi\omega_s)\int_{-\infty}^{+\infty} \chi'' \cos\omega_d t \, d\omega_d. \tag{1b}$$

One never knows $\chi(\omega_d)$ completely, and thus one cannot deduce $\psi(t)$ from these equations. Grant[4] has pointed out that some assumption has to be made anyhow about the shape of $\chi(\omega_d)$ or $\psi(t)$. Therefore, the normal procedure is to define some parameters of $\psi(t)$, which are theoretically obtainable, and which one may determine then by investigating $\chi(\omega_d)$.

We summarize these parameters and their relations to parameters of $\chi(\omega_d)$:

1. The *g factor* gives the position of ω_s on the ω axis. It determines how to "transform" the relaxation function to $\psi(t)$.
2. The *linewidth* gives the region over which χ is extended along the ω axis. It is proportional to the inverse of the characteristic time τ of $\psi(t)$. The proportionality factor depends on the definition of "linewidth" in χ and the definition of "relaxation time" in $\psi(t)$.
3. The *area under the absorption curve* $\chi''(\omega_d)$ gives the value of $\psi(0)$, and hence the *static susceptibility* χ_s. We will derive in this paper an equivalent parameter for the dispersion curve $\chi'(\omega_d)$.
4. The *moments* of $\chi''(\omega_d)$ give the derivatives of $\psi(t)$ for t approaching zero, and hence a *Taylor expansion* of $\psi(t)$. The whole (infinite) set of moments of χ'' would yield us $\psi(t)$ completely of course; however, as proved by Grant,[4] without some previous assumptions even the first *hundred* moments do not teach us *anything* about the shape of $\psi(t)$. Here too we will introduce equivalent parameters for the dispersion curve.

B. *g* Factor and Linewidth

As a matter of fact it is immaterial—from a purely theoretical point of view—whether one considers, for determining the first two parameters, the absorption or the dispersion. In order to measure the g factor one can make use of the maximum in χ'' as well as of the central inflection point or the zero point in χ'. The linewidth can be found from χ' or from χ''.

It remains to discuss the integrals of χ''.

C. Static Susceptibility

The static susceptibility χ_s is given quite generally by

$$\chi_s = \lim_{t\to 0}\psi(t).$$

With Eq. (1b) we get the well-known relation:

$$\chi_s = (2/\pi\omega_s)\int_{-\infty}^{+\infty} \chi'' \, d\omega_d = \lim_{\omega_d\to\infty} (2/\pi\omega_s)\int_{-\omega_d}^{+\omega_d} \chi''(\omega_d')\, d\omega_d'. \tag{2}$$

It must be emphasized that Eq. (2) supposes the integral of Eq. (1b) to be convergent, and hence the *Kramers-Kronig relations to be valid.*

We use Eq. (1a) to deduce another *quite new* expression for χ_s. Let us write down Eq. (1a) in a slightly modified form:

$$\psi(t) = (4/\pi\omega_s)\left[\int_0^N -\chi' \sin\omega_d t\, d\omega_d + \int_N^\infty -\chi'\omega_d \frac{\sin\omega_d t}{\omega_d} d\omega_d\right]. \tag{3}$$

In the limit $t \to 0$ the first integral vanishes, whatever the (fixed) positive value of N, for, in any case:

$$|\sin\omega_d t| < \omega_d t,$$
$$|\chi'| < \infty,$$
$$0 \leqslant \omega_d \leqslant N < \infty.$$

For the calculation of the second integral we first derive the following identity by applying the same reasoning together with Dirichlet's integration (A is a constant):

$$\lim_{t\to+0}\int_N^\infty A\frac{\sin\omega_d t}{\omega_d} d\omega_d = \lim_{t\to+0}\int_0^\infty A\frac{\sin\omega_d t}{\omega_d} d\omega_d = (\lim_{t\to+0} A)\frac{\pi}{2} = \tfrac{1}{2}\pi A. \tag{4}$$

Now, suppose that

$$L \equiv \lim_{\omega_d\to\infty} (\chi'\omega_d)$$

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[2] R. Kubo and K. Tomita, J. Phys. Soc. Japan **9**, 888 (1954).

[3] J. Talpe, thesis, Leuven, 1964, p. 100 (unpublished).

[4] W. J. C. Grant, Physica **30**, 1433 (1964).

exists and is finite. Then, for t approaching zero, the second integral of Eq. (3) approaches $-\frac{1}{2}\pi L$, since, for $\omega_d > N$, the difference $(\chi'\omega_d - L)$ becomes negligible compared with L (N being chosen high enough). Thus, if the limit exists and is finite

$$\chi_s = \lim_{\omega_d \to \infty} (-2\chi'\omega_d/\omega_s). \tag{5}$$

For evaluating χ_s, Eq. (5) can be applied as well as Eq. (2). Moreover, a simple check of the convergence of the two limits in the case of a Lorentzian line illustrates already the improvement of Eq. (5) over Eq. (2):

Equation (2) converges as

$$1-(2/\pi)x^{-1}+(2/3\pi)x^{-3}-\cdots;$$

Equation (5) converges as $1-x^{-2}+x^{-4}-\cdots$.

Other advantages of the use of Eq. (5) will be indicated below.

D. Taylor Expansion of the Relaxation Function

Successive differentiation of Eq. (1b) with respect to t, while taking the limit for t approaching zero, yields the well-known expressions for the moments of the absorption line. We confine ourselves to the even moments, the odd ones being zero:

$$\psi^{(2n)}(0) = (-1)^n (2/\pi\omega_s) \int_{-\infty}^{+\infty} \chi''\omega_d^{2n}\, d\omega_d.$$

Here the restrictions about convergence for χ'' are still more stringent, and for a Lorentzian line, for example, the formula breaks down.

Let us use again Eq. (1a). Successive differentiation of this equation with respect to t yields

$$\psi^{(2n)}(t) = (-1)^n (2/\pi) \int_{-\infty}^{+\infty} \frac{-\chi'\omega_d}{\omega_s}\omega_d^{2n}\frac{\sin\omega_d t}{\omega_d}\, d\omega_d. \tag{6}$$

Now suppose $(\chi'\omega_d)$ to have an asymptotic expansion[5,6]:

$$-\chi'\omega_d/\omega_s \equiv a_0 + a_2\omega_d^{-2} + a_4\omega_d^{-4} + \cdots + a_{2k}\omega_d^{-2k} + R_{2k}, \tag{7}$$

with, for any (fixed) non-negative integer value of k:

$$\lim_{\omega_d \to \infty} R_{2k}\omega_d^{2k} = 0.$$

By this asymptotic expansion Eq. (6) is transformed [using again Eq. (4) and assuming $k=n$] to

$$\psi^{(2n)}(t) = (-1)^n 2a_{2n} + (-1)^n (2/\pi) \times \sum_{k=1}^{n} 2\int_0^{\infty} a_{2n-2k}\omega_d^{2k}\frac{\sin\omega_d t}{\omega_d}\, d\omega_d + (-1)^n 2Q_{2n}/\pi, \tag{8}$$

where

$$Q_{2n} \equiv \int_{-\infty}^{+\infty} R_{2n}\omega_d^{2n}\frac{\sin\omega_d t}{\omega_d}\, d\omega_d.$$

In the same way as in the preceding paragraph it can be shown that

$$\lim_{t\to 0} Q_{2n} = 0.$$

Let us consider furthermore the summation term of Eq. (8). On the terms of this sum the following general remark can be put forward: The integral

$$\mathcal{I}_k \equiv \int_N^{N_1} a_{2n-2k}\omega_d^{2k}\frac{\sin\omega_d t}{\omega_d}\, d\omega_d \quad \text{with} \quad N_1 > N$$

is an oscillating function of N_1. Its value is determined by the phase of $(N_1 t)$ in the sine and hence the frequency is of the order of N_1. The amplitude is of the order of $a_{2n-2k}N_1^{2k}$. But for t less than a certain value t_1, the term with Q_{2n} in Eq. (8) is negligible with respect to $\psi^{(2n)}(t)$ and a_{2n}. Therefore, if the asymptotic expansion exists, the limit of $\mathcal{I}_k$ for $N_1 \to \infty$ has to be taken in an unambiguous way and must become independent of t for $t \to 0$. The only way to realize these conditions is that

$$\lim_{t\to 0}\left(\lim_{N_1\to\infty} \mathcal{I}_k\right) = 0.$$

Finally Eq. (8) reduces thus to the simple relation

$$\psi^{(2n)}(+0) = (-1)^n 2a_{2n}.$$

So we have shown that the derivatives of $\psi(t)$ in the limit for t approaching zero are essentially the coefficients of the asymptotic expansion of χ'. A simple check shows that this statement holds, not only for a Gaussian shape,[7] but also, for example, for a Lorentzian shape. The equivalence between the moments and the coefficients of the asymptotic expansion of respectively two functions, connected by what we now call the Kramers-Kronig relations, was already demonstrated in 1895 by Stieltjes[8] in his theorem of moments. It must be pointed out, however, that his theorem is only valid for finite moments,[9] while our statement includes also the case of infinite moments, e.g., the Lorentzian line.

II. SOME GENERALIZATIONS

In this second part we will examine three cases where the resonance lines are not so simple and tractable as assumed in the foregoing section:

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[5] A. Angot, *Compléments de Mathématiques* (La revue d'optique théorique et instrumentale, Paris, 1961), p. 335.

[6] H. Poincaré, Acta Math. **8**, 295 (1886).

[7] The surprising discovery of such a relation, while calculating the asymptotic expansion of a Gaussian dispersion line, was in fact the beginning of the story of this section.

[8] T. J. Stieltjes, Ann. Fac. Sci. Univ. Toulouse Sci. Math. Sci. Phys. **8**, J1-122 (1894); **9**, A1-47 (1895).

[9] Even with the refinements introduced by Hamburger [H. Hamburger, Math. Ann. **81**, 235 (1920)].

First, when the HF field is so strong that saturation is no longer negligible; second, when the resonance field does not greatly exceed the linewidth; and finally, when the resonance line is composite and hence asymmetric or even split up.

Note: As we are getting closer to the experimental conditions, we will from now on consider the frequency as a constant, denoted by ω or by ω_0: $\omega \equiv \omega_0$, and the static magnetic field B_s as variable, the resonance value of which is denoted by B_0: $\omega_0 \equiv -\gamma B_0$. We do not discuss here corrections due to Eq. (9b) below, although they may easily influence the linewidth measurements by 10%.[10] This type of correction, however, is insignificant for static-susceptibility measurements. For high fields we have

$$\omega_d \equiv \omega - \omega_s \equiv \omega_0 - \omega_s = (-\gamma B_0) - (-\gamma B_s) = \gamma (B_s - B_0) \equiv \gamma B_d.$$

A. Saturation

Absence of saturation (i.e., linearity), together with the other conditions necessary for the Kramers-Kronig relations to be valid, guarantee the validity and even the convergence of Eq. (1a) and (1b). However, when saturation appears, these relations fail, and we have to appeal to the Bloch theory, e.g., to see what happens.

For discussions about the linewidth and the g factor, as measured on the absorption line, we refer to the work of Van Gerven.[11] It would be of interest to do a similar job for the dispersion line.

As for the static susceptibility, it can be shown easily that Eq. (2) breaks down in the presence of saturation. Equation (5) however remains valid, but the convergence of the limit depends now (also) upon the amplitude of the HF field. As a matter of fact, in the case of complete saturation the use of χ'' becomes absolutely impossible, the absorption being zero, while Eq. (5) still remains useful under certain conditions, as, for example, in some of the circumstances indicated by Solomon and Ezratty[12] (see Talpe[13]).

B. Linewidth of the Order of the Resonance Field

The transformation which eliminates the resonance frequency from the relaxation function, leading to Eqs. (1a) and (1b), assumes the static resonance field B_0 to be much larger than the (half) linewidth δ. If δ is of the order of B_0, everything about the line shapes becomes very complicated. As to the absorption, this case has been discussed extensively by Van Gerven[11] by means of the so-called "modified Bloch theory." It might be worthwhile to do the same for the dispersion.

There exists, however, another procedure, namely, reducing the static field to zero and using a low-frequency field. (In this way, of course, one cannot determine g factors.) As a matter of fact, the static susceptibility is exactly the "dispersion" in zero field. The experimental problem then is to apply a large enough sweep in order to obtain the zero level $\chi'(\infty)$ of the signal. Anyway, one cannot use Eq. (2).

For the discussion on the width of the absorption line we refer to the quoted publication[11]—to be supplemented in an analogous fashion for the dispersion line.

C. Composite Line

An asymmetric resonance line or a split line can be considered quite generally as the resultant of a group of elementary lines. The paramagnetic-resonance line of a powdered sample of diphenylpicrylhydrazyl (DPPH), e.g., which is very asymmetric (see Fig. 1), is a sum of individual symmetric lines, produced by crystals in various directions. Sometimes a finite number of lines is assembled, each coming from the spins that have a certain definite position and identity in the substance. Or even transitions from the same kind of spins between different levels, as in the case of electric quadrupole splitting in NMR, may produce a composite line. But, anyhow, the elementary lines are symmetric[14] (if we suppose, as we do, that the linewidth is much smaller than the static-field values used: $\delta \ll B_0$). A lot of work has been done up to now to disentangle such composite lines. For a 1963 review we refer to the paper of Drăghicescu.[15] When one is interested precisely in the splitting, the only thing to do in general is to try to locate the different lines and to evaluate the relative intensities. Let us emphasize that

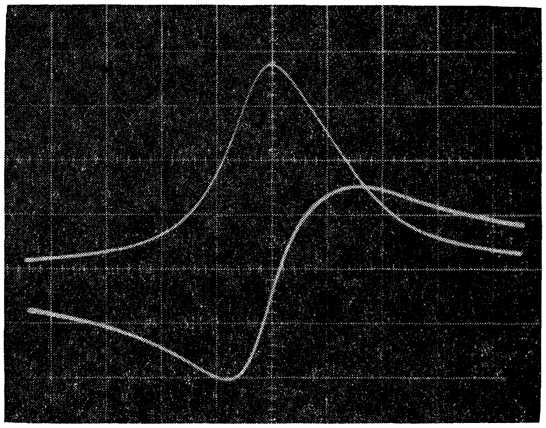

FIG. 1. Dual-beam oscillogram of an experimental ESR dispersion and absorption line at 9 GHz from a sample of 7.38 mg DPPH powder at 291°K. Total width of the trace: 0.90 mT (=9.0 G). Total height of the dispersion line: 0.466 mm³. The static field increases from left to right.

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[10] Reference 3, p. 123.

[11] L. Van Gerven, *Lijnvormen in Paramagnetische Resonantie* (Interuniversitair Instituut voor Kernwetenschappen, Brussels, 1963).

[12] I. Solomon and J. Ezratty, Phys. Rev. **127**, 78 (1962).

[13] Reference 3, p. 124.

[14] A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon Press, Oxford, England, 1961), p. 108.

[15] P. Drăghicescu, Studii Cercetări, Inst. Fizică **14**, 201 (1963).

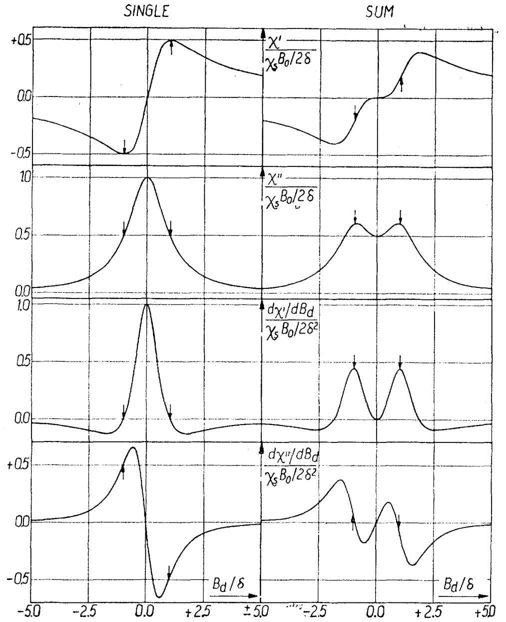

FIG. 2. Comparison of χ', χ'', $d\chi'/dB_d$, and $d\chi''/dB_d$ for one single Lorentzian line and for the sum of two Lorentzian lines separated by a distance in field equal to the linewidth at half-height 2δ. The small vertical arrows indicate $B_d = \pm\delta$.

one gets a much clearer spectrum when recording the derivative (with respect to the static field) of the dispersion line than that of the absorption line. The derivative of $\chi'(B_d)$ has a sharp maximum in its center and very weak tails. In Fig. 2 the comparison is made between χ', χ'', $d\chi'/dB_d$, and $d\chi''/dB_d$ for a single Lorentzian line and for the sum of two equal Lorentzian lines, situated at a distance of one linewidth at half-height from each other.

If the paramagnetic system is linear, one can of course use Eq. (2) for evaluating the static susceptibility from the composite line. But Eq. (5) also is still valid. Moreover, if the composite line is not too asymmetric, one may prove (at least for the case that the elementary lines are Lorentzian) that for the same *relative* amplitude of the modulation field B_r [see Eq. (10)] the convergence of Eq. (5′) below becomes even better.

III. EXPERIMENTAL PRINCIPLES AND METHODS APPLIED WHEN USING DISPERSION INSTEAD OF ABSORPTION

A. Introduction

It is well known how in communication techniques an important improvement is reached by using frequency modulation instead of amplitude modulation. Absorption measurements concern an amplitude variation, while dispersion has essentially to do with the frequency. We will point out now the *experimental* advantages of measuring dispersion instead of absorption.

The experimental work, by which the following ideas are supported, is done on a microwave dispersion spectrometer, described elsewhere.[16] The spectrometer contains a stabilization system, locking the klystron frequency ω_0 to the "eigenfrequency" ω_c of the sample cavity.

The absorption brings about a change in the "eigendamping" $1/Q_0$ of this cavity:

$$\eta\chi'' = \Delta(1/Q_0), \tag{9a}$$

and is measured in a conventional way. η is the filling factor of the sample in the cavity (we use rationalized mksa units, hence 4π disappears).

The dispersion brings about a change in the eigenfrequency of the cavity, which equals the change in actual frequency of the klystron, because of the stabilization. It is this *change in* ω_0, being proportional to χ', which we *measure*:

$$\eta\chi' = -2\Delta\omega_c/\omega_c = -2\Delta\omega_0/\omega_0. \tag{9b}$$

A more detailed analysis of the results given in Eqs. (9a) and (9b)—including the discussion of HF demagnetizing effects—is elaborated in the thesis of Talpe.[17]

B. *g* Factor and Linewidth

The quality of the measurements of the two parameters concerning the frequency axis—or, more practically, the magnetic field axis—depends in first order on how well one can keep constant and measure a frequency and a magnetic field. When one wants to determine the place on this axis of some zero point or some maximum of a line, the linearity of the apparatus is of no importance. However, when measuring the width of an absorption line—either the width at half-height or the width between the inflection points—the linearity of the apparatus is important, and, moreover, for the first case it is necessary to know exactly the signal level at zero absorption. Both these problems, which are often very annoying, disappear in dispersion measurements. For *g* factor measurements we see no direct advantage either in using absorption or in using dispersion.

C. Static Susceptibility

The advantage of using the dispersion appears most explicitly when measuring static susceptibilities. We shall assume from now on that both Eqs. (2) and (5),

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[16] Mededel. Koninkl. Vlaam. Acad. Belg., Kl. Wetenschap. (to be published).

[17] Reference 3, p. 8.

transposed here to variable field (near resonance $B_s \cong B_0$)

$$\chi_s = \lim_{B_d \to \infty} (2/\pi B_0) \int_{-B_d}^{+B_d} \chi''(B_d')\, dB_d', \qquad (2')$$

$$\chi_s = \lim_{B_d \to \infty} (2\chi' B_d / B_0), \qquad (5')$$

hold equally, although Eq. (5′) is more convergent and more generally valid than Eq. (2′), as shown in detail above.[18]

The application of each of these formulas requires that the spectrometer be *linear*; furthermore, it requires a *calibration* of the signal, and finally some *approach to a limit.*

1. Linearity and Calibration of the Spectrometer

With our spectrometer,[16] which contains a very elegant device for checking its linearity accurately, we found it much easier to achieve linearity in the dispersion mode than in the absorption mode, essentially because our dispersion measurements are based on a null method.

Calibration of the dispersion signal is quite easy and can be made in an absolute way with our type of spectrometer. The only thing to be done is to measure the frequency of the klystron at the points where χ' has its maximum and minimum. The filling factor can be determined accurately. In practice we obtain an accuracy of a few percent. For experimental details we refer to the paper describing the spectrometer.[16] As a matter of fact this facility of calibration is *not* limited to *microwave* dispersion spectrometers.

Calibration of an absorption signal requires in general the measurement of an HF energy difference and of an HF coupling, connecting the change in damping to the change in measured energy. In practice the only experimental method to carry out such measurements with a precision higher than 50% consists in using some reference substance of known susceptibility. However, one should pay attention to the change in coupling when changing samples: variations of 100% are quite normal! It is feasible to measure those elements of the coupling that are most influenced by the sample itself. But nevertheless, this remains an inaccurate procedure, and generally one prefers some method in which both samples are together in the HF apparatus. Great care must be taken then to avoid mixing of the sample signal and the reference signal. Anyhow, the problem remains of finding a good reference: stable and having an accurately known susceptibility at each temperature. We shall not digress upon that point now, but some remarks ought to be made. Of the two most studied reference substances—DPPH and charred dextrose—DPPH is certainly not a good one for ESR,[19] and for charred dextrose it is difficult to predict the number of spins, as this number depends very critically on the treatment temperature and the vacuum conditions during the charring process.[19] The use of NMR to calibrate an ESR spectrum is restricted to very few cases.[19]

2. Approach to the Limit

The application of Eq. (2′) requires an integration, or, in case the derivative of the absorption curve is recorded, a double integration or at least a moment calculation, the latter by virtue of an integration by parts:

$$\int_{-\infty}^{+\infty} \chi''\, dB_d = (\chi'' B_d)_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty} B_d\, d\chi''$$

$$= -\int_{-\infty}^{+\infty} \frac{d\chi''}{dB_d} B_d\, dB_d.$$

Whatever the electronic[20,21] or mechanical[22] tricks used for these integrations, it remains a very important source of trouble, starting—for the simple integration—with the uncertainty about the zero level, and ending nowhere.

For determining the limit of the product in Eq. (5′), on the contrary, there exists a very simple and accurate method, which we will present here.

Upon the constant field B_0, centered on the central inflection point (or the zero point) of $\chi'(B_s)$, we superpose a sinusoidal modulation field $b_r = B_r \cos\Omega t$:

$$B_s = B_0 + B_r \cos\Omega t;\; B_d = B_r \cos\Omega t. \qquad (10)$$

χ' is displayed on an oscilloscope, whose horizontal deflection is sinusoidal with the same frequency Ω and with a variable phase φ with respect to b_r.

Let us take first $\varphi = 0$ (see Fig. 1, dispersion line). Now the horizontal oscilloscope axis is a field axis, going from $B_d = -B_r$ to $B_d = +B_r$. B_0 and B_r are known. We have only to measure the *difference* in χ' at both ends of the horizontal axis, and multiply this difference by the modulation amplitude over the resonance field, to get

$$P(B_r) \equiv 2\chi'(B_r) B_r / B_0. \qquad (11)$$

This expression is exactly the product given in Eq. (5′), with $B_d = B_r$. When we take B_r larger and larger, we observe a nice approach to a limit for P (Fig. 3). For a Lorentzian line the error $(1 - \chi_s/P)$ equals -1% for $B_r = 10\delta$, where 2δ is the width between maximum and minimum of χ'. For a Gaussian line the error amounts in these conditions to $+1\%$. Generally the error lies somewhere in between these two values.[23] The centering of the static field on the resonance value B_0 is not very critical, since the biggest part of the resulting error is

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[18] For $B_r = 10\delta$ [see Eq. (10) below] the error is theoretically equal to 7% for Eq. (2′) and to 1% for Eq. (5′).

[19] Reference 3, p. 177.

[20] J. Hervé, Compt. Rend. **244**, 1475 (1957).

[21] J. Hervé, Compt. Rend. **245**, 653 (1957).

[22] V. R. Burgess, J. Sci. Instr. **38**, 98 (1961).

[23] Experimentally we observe indeed a much better convergence.

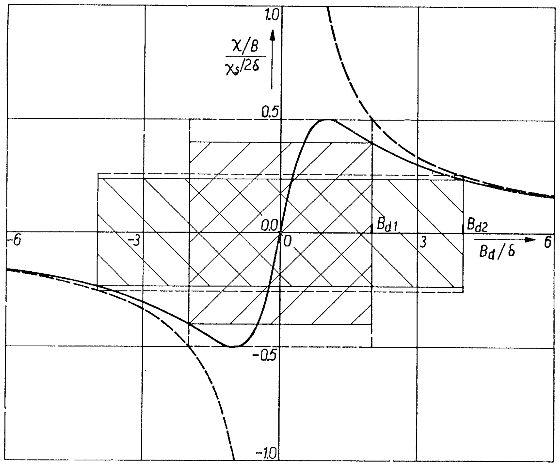

FIG. 3. Approach to the limit of the product $P(B_r) \equiv 2\chi' B_r/B_0$. Full curve: χ'/B_0 as a function of B_d ($\chi \equiv \chi'$; $B \equiv B_0$). Dashed curve: $\chi_s/2B_d$ as a function of B_d ($\chi \equiv \chi_s$; $B \equiv 2B_d$). Surface $/\!/\!/ = 2\ P(B_{d1})$. Surface $\backslash\!\backslash\!\backslash = 2\ P(B_{d2})$. The limit equals half the area of the rectangles inscribed in the hyperbola.

compensated just by taking the double difference in χ', namely $\chi'(B_r) - \chi'(-B_r)$ and not $\chi'(B_r) - \chi'(0)$. By this very procedure also an exact knowledge of the signal zero level becomes completely superfluous.

The experimental method for measuring P goes as follows. We consider the dispersion line as represented on the oscillogram of Fig. 1. Now we shift the phase φ to $\pi/2$. The two values $\chi'(B_r)$ and $\chi'(-B_r)$, between which we want to measure the difference, are now exactly one above the other in the middle of the oscilloscope pattern, as shown in Fig. 4. The difference can be measured directly in volts. A method for measuring such differences on an oscilloscope screen with a 0.2% precision is described in another paper.[16] All we need further is a calibration of voltage versus frequency. Therefore we adjust the phase φ so as to get the maximum of one trace above the minimum of the other trace (see Fig. 5), and we measure again the difference in volts. Afterwards we measure this same difference (now as a frequency difference) directly in Hz. In case the latter difference is too small, we apply a known artificial frequency modulation for intermediate calibration.

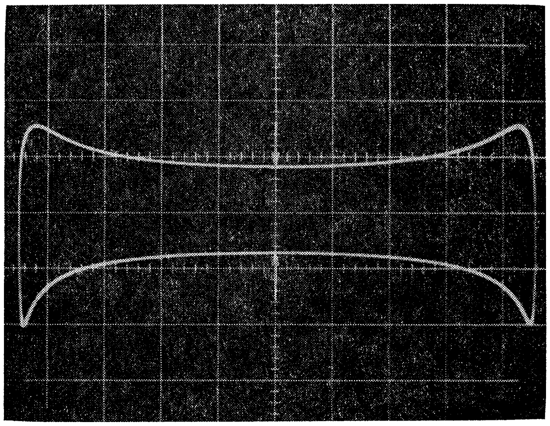

FIG. 4. The ESR dispersion-line oscillogram of Fig. 1, now with the horizontal sweep $\pi/2$ out of phase with respect to the modulation field ($\varphi = \pi/2$), as used for measuring the difference between $\chi'(B_r)$ and $\chi'(-B_r)$, i.e., the vertical distance between the two "tails" of the dispersion line.

Note: When the derivative of the dispersion line is recorded, we can use for the determination of χ_s a relation, analogous to Eq. (5′), that will not be derived here[24]:

$$\chi_s = \lim_{B_d \to \infty} \left[-2(d\chi'/dB_d) B_d^2 / B_0 \right].$$

It is useful for broad lines.

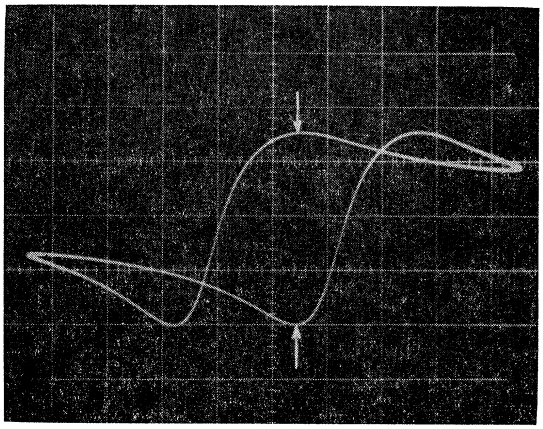

FIG. 5. The ESR dispersion-line oscillogram of Fig. 1, now with the horizontal sweep somewhat out of phase, just the right amount for measuring the difference between $\chi'_{\max}$ and $\chi'_{\min}$. Each of both traces is brought about during one of the two half-periods of the modulation field.

D. Moments and Asymptotic Expansion

The calculation of the derivatives of the relaxation function in the limit $t \to 0$ is sometimes possible on theoretical grounds. In practice, however, only the second and the fourth derivatives are calculated. On the other hand, the experimental determination of the fourth and higher moments of an absorption line is quite a problem also. Even the second is already hard to determine. Some electronic tricks[20,21] can be helpful, but even then it remains necessary to have at one's disposal a very accurately traced line.

The determination of the coefficients of the asymptotic expansion is also rather complicated, but it can be carried out by iteration. Suppose χ_s, and hence a_0 of Eq. (7), has been measured. From Eq. (7) we get (transposed to variable field)

$$a_2 = \lim_{B_d \to \infty} (\chi' B_d / B_0 - a_0) \gamma^2 B_d^2.$$

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[24] Reference 3, p. 108.

This means that we have to evaluate the difference between the curve χ'/B_0 and the hyperbola a_0/B_d (see Fig. 3), and to multiply it by $\gamma^2 B_d^3$. The precision depends on the accuracy with which the tails of the curve are recorded. Here again we have similar advantages in utilizing the dispersion to those in the measurement of χ_s. There are analogous formulas for differentially recorded lines: one has only to differentiate Eq. (7), after having divided it by ω_d and transposed it to variable field.[24]

IV. SOME TEST MEASUREMENTS

In order to test our dispersion method we performed a series of measurements in our 9-GHz ESR spectrometer.[16] We shall discuss only the measurement of the static susceptibility, which constitutes the most interesting feature of the method. Two types of samples of α, α'-diphenyl, β-picrylhydrazyl (DPPH) were used, both prepared from a fine powder of triclinic DPPH crystals, supplied by A. G. Fluka, Buchs (Switzerland). Samples of the first type (A) were simply sealed off in a small thin-walled glass tube. Those of the other type (B) were rinsed three times with helium gas, pumped off afterwards by means of active charcoal, and finally sealed off *in vacuo.*

A. Results

Room-temperature measurements of χ_s on the *same sample*, separated by a couple of months and by a complete detuning and deregulation of the microwave spectrometer, gave the same result within less than 1%. Room-temperature measurements on different samples of the *same type* (differing in weight) also gave the same result within about 1%. During these measurements the temperature of the sample is kept at a constant value ±0.3°C by means of a thermostatted bath of water. Absolute comparisons of the results for all the various samples are difficult to make, because of the uncertainty in the actual value of χ_s for a given sample (see below).

TABLE I. The static mass susceptibility χ_s/ρ (and its inverse) of DPPH, as measured by the resonance-dispersion method, as a function of temperature (ρ = the density of DPPH).

Sample	T (°K)	χ_s/ρ (mm^3/kg)[a]	ρ/χ_s (g/mm^3)[a]
A	290.8	35.5	28.2
	77.4	106	9.43
	74.1	108	9.26
	70.6	112	8.93
	65.8	118	8.47
	20.4	274	3.65
	17.9	295	3.39
	15.1	309	3.24
B	295.0	28.3	35.3
	77.4	93.2	10.7
	66.1	102	9.80
	20.4	224	4.46
	17.9	243	4.12
	15.1	271	3.69

[a] We use rationalized mksa units.

TABLE II. The static mass susceptibility χ_s/ρ (and its inverse) of DPPH, as measured by Van Itterbeek and Labro using a static method, as a function of temperature (calculated from data of Ref. 25).

Sample	T (°K)	χ_s/ρ (mm^3/kg)[a]	ρ/χ_s (g/mm^3)[a]
I	294.0	29.2	34.3
	77.4	90.1	11.1
	70.0	97.1	10.3
	62.9	105	9.53
	20.4	244	4.09
	18.0	270	3.71
	16.6	289	3.46
	14.7	327	3.06
III	295.0	35.8	27.9
	77.4	114	8.75
	69.9	123	8.12
	63.0	133	7.50
	20.4	312	3.21
	18.0	342	2.92
	16.6	364	2.75
	14.4	410	2.44

[a] We use rationalized mksa units.

Further measurements were done at liquid-nitrogen and liquid-hydrogen temperatures. The experimental results are collected in Table I.

We have compared our resonance-dispersion results with the results of Van Itterbeek and Labro,[25] who have measured by means of a static method (the Faraday or balance method) the static susceptibility of two samples—listed samples I and III—of triclinic DPPH. Sample I, prepared in the laboratory, was several years old by the time of the measurements. Sample III is of the same origin (Fluka) as our samples A and B. For comparison we have shown their values, in mksa units, in Table II.

B. Discussion

At *all* temperatures, except perhaps in the very coldest part of the liquid-hydrogen region, the experimental results on sample B are in close agreement with a Curie-Weiss law

$$\chi_s^{-1} \propto (T-\theta)$$

yielding a Curie temperature θ of (-19 ± 1)°K (see Fig. 6). The same Curie temperature of -19°K, but a different Curie constant, is found for sample A, if one neglects the liquid-nitrogen points (full line in Fig. 6). These latter points yield a quite different (spurious) Curie temperature of -31°K (dashed line in Fig. 6).

In the same graph of Fig. 6 we also check the results of the static measurements of Van Itterbeek and Labro against a Curie-Weiss law: once neglecting the liquid-nitrogen points, and once taking them into account. Without the liquid-nitrogen points a common Curie

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[25] A. Van Itterbeek and M. Labro, Physica 30, 157 (1964).

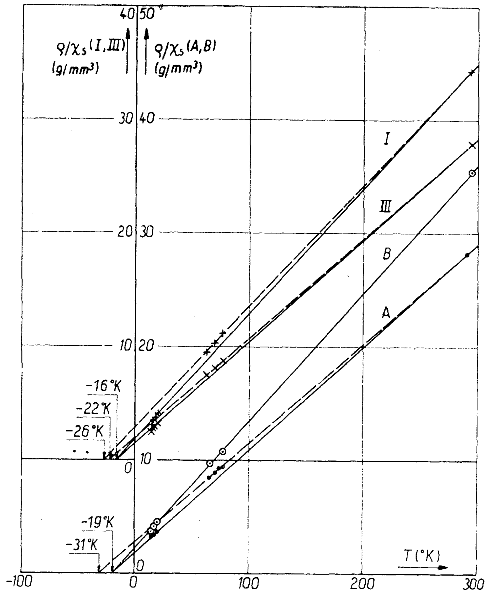

FIG. 6. The inverse of the static mass susceptibility of DPPH as a function of temperature. ● Dispersion measurements on a nonrinsed sample (A). ⊙ Dispersion measurements on a rinsed sample (B). + Static measurements by Van Itterbeek and Labro (Ref. 25) on a nonrinsed aged sample (I). × Static measurements by the same authors on a nonrinsed sample (III). ——Curie-Weiss curves through the room-temperature and liquid-hydrogen-temperature points. - - - -Curie-Weiss curves through the room-temperature and liquid-nitrogen-temperature points. At left the respective Curie points are indicated. For clarity the vertical scales for samples A, B and I, III are shifted. Rationalized mksa units are used.

temperature of −16°K is found, while otherwise divergent "Curie temperatures" are found.

The divergences in θ, occurring for all samples except the "rinsed" sample B, could be explained by assuming an anomalous lowering of χ_s in the liquid-nitrogen region, due to the presence of air around the samples. Analogous effects are found in coal. This would also explain the important disagreement about the Curie temperature of DPPH existing in the literature,[25] for this parameter is being determined mostly by extrapolation from measurements at room temperature and liquid-nitrogen temperatures.

Finally, if we consider the slope of the lines on the graph of Fig. 6, we could perhaps say that aging the sample has the same effect as pumping off the air. But here the experimental basis is really too small to draw conclusions from.

After all, the most striking result of the test measurements, reported here, is to be found in the perfect reproducibility of the susceptibility measurements, realized without any critical spectrometer regulation or calibration.

V. GENERAL CONCLUSIONS

From a theoretical as well as from an experimental standpoint, magnetic-resonance dispersion constitutes in many cases a much more valuable tool for studying paramagnetic systems than magnetic-resonance absorption. Simple and accurate determination of the static susceptibility—or spin density—of such systems, without integration procedures or reference substances, may be mentioned as a most interesting application of resonance-dispersion measurements.

Last, but not least, it ought to be emphasized that this method, being a *resonance* method, permits *selective* and *sensitive* measurements of the susceptibility of paramagnetic systems:

Selective measurements on complex or impure samples, for example, in the (frequent) case of contamination by ferromagnetic impurities, a most serious problem when using static nonselective methods;

sensitive measurements on feebly paramagnetic systems, embedded in strongly paramagnetic or diamagnetic substances, as for example nuclear spin systems. The resonance-dispersion method is applicable, of course, as well in radiospectroscopy (NMR) as in microwave spectroscopy (ESR).

ACKNOWLEDGMENTS

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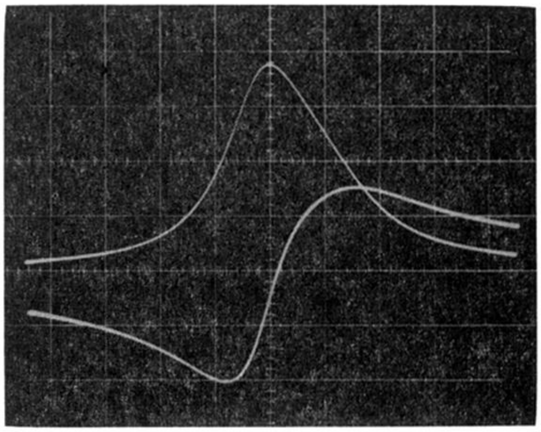

FIG. 1. Dual-beam oscillogram of an experimental ESR dispersion and absorption line at 9 GHz from a sample of 7.38 mg DPPH powder at 291°K. Total width of the trace: 0.90 mT (=9.0 G). Total height of the dispersion line: 0.466 mm^3. The static field increases from left to right.

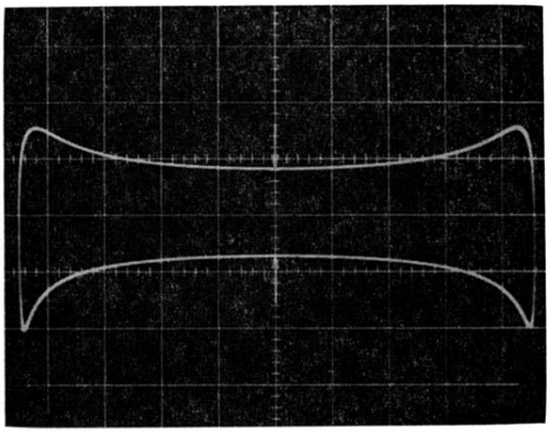

FIG. 4. The ESR dispersion-line oscillogram of Fig. 1, now with the horizontal sweep $\pi/2$ out of phase with respect to the modulation field ($\varphi=\pi/2$), as used for measuring the difference between $\chi'(B_r)$ and $\chi'(-B_r)$, i.e., the vertical distance between the two "tails" of the dispersion line.

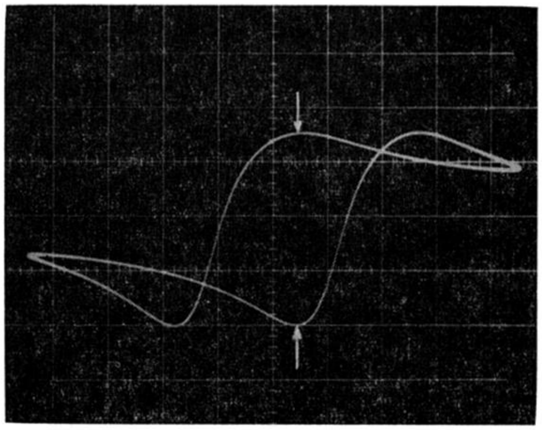

FIG. 5. The ESR dispersion-line oscillogram of Fig. 1, now with the horizontal sweep somewhat out of phase, just the right amount for measuring the difference between $\chi'_{\max}$ and $\chi'_{\min}$. Each of both traces is brought about during one of the two half-periods of the modulation field.