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Paramagnetic Resonance Detection along the Polarizing Field Direction

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Strong rf power, modulated at a low frequency, was applied to a paramagnetic solid (diphenyl pycril hydrazil) in a dc field H_z of up to 20 gauss. The resulting changes in M_z at the modulation frequency produced a voltage in a coil oriented in the z direction, to provide a measure of M_z. A sensitive test of the equation of motion of the spin magnetization was achieved by using 19.5-Mc/sec circularly polarized rf of up to 6 gauss in the x-y plane, square wave modulated at 280 cps. The observed 280-cps signal was consistent with the Bloch equations, assuming relaxation toward the instantaneous applied magnetic field. As predicted, M_z was not zero when $H_z=0$. A Bloch-Seigert effect was also observed.

I. INTRODUCTION

In his original paper on nuclear induction Bloch[1] suggested phenomenological equations of motion for nuclear magnetization. It has generally been assumed that Bloch's equations also apply to electronic spin magnetization in those solids which exhibit Lorentzian magnetic resonance lines as a result of strong exchange interaction between spins.

Several writers[2,3] have pointed out that it is reasonable to modify the Bloch equations so that the relaxation terms make the magnetization tend to approach its equilibrium value with respect to the instantaneous applied magnetic field instead of the fixed field. Such a modification is theoretically preferable.[4–6] When the relaxation times T_1 and T_2 are equal, as is observed in diphenyl pycril hydrazil, and as is expected in general at low fields (if the Bloch equations are valid at all), these modified Bloch equations are:

$$\partial \mathbf{M}/\partial t=\gamma \mathbf{M}\times\mathbf{H}-(\mathbf{M}-\chi_0\mathbf{H})/T_1, \qquad (1)$$

where $\mathbf{H}$ is the magnetic field, χ_0 the spin susceptibility, and γ the gyromagnetic ratio. The "unmodified" Bloch equations are the same as (1) except that $\chi_0\mathbf{H}$ is replaced by $\chi_0 H_z\mathbf{k}$, where $\mathbf{k}$ is a unit vector in the z direction (fixed field direction). The modified Bloch equations (1) are consistent with experiments in metals[7] and organic free radicals[2,8] when the applied radiofrequency magnetic field is small. The form (1) is also consistent with observed[9] Debye dispersion in paramagnetic solids.

Both the modified and unmodified Bloch equations can be solved exactly[8] when a fixed field H_z and a perpendicular circularly polarized rf field H_1 are applied to the solid. For the steady state, the modified Bloch equations predict that the magnetization in the fixed-field direction is

$$M_z=\frac{(\Delta\omega T_1)(\gamma H_1T_1)\chi_0H_1+[1+(\Delta\omega T_1)^2]\chi_0H_z}{1+(\Delta\omega T_1)^2+(\gamma H_1T_1)^2}, \qquad (2)$$

where $\Delta\omega$ is the frequency deviation from resonance, $\gamma H_z-\omega$.

It is noteworthy that (2) is not zero when H_z, the fixed field, is zero. In other words, a circularly polarized rf field alone can produce a stationary component of magnetization perpendicular to the plane in which the rf field rotates. This can be understood physically by considering a spin which has just relaxed along the instantaneous rf field direction. As the field rotates, the spin is unable to follow it, and at a later time there will be an angle between the spin and the rf field. The spin will then precess around the rf magnetic field, out of the plane of rotation of the field, and will contribute to a stationary magnetization perpendicular to this plane.

This paper reports measurements of the stationary component of magnetization M_z resulting from a fixed field H_z plus a perpendicular linearly or circularly polarized rf field. This magnetization is made observable by amplitude-modulating the rf field; the resulting changes in M_z induce a voltage in a coil whose axis is in the z direction. This method has the advantage that the pickup system is tuned to detect a frequency very different from that of the rf field. This technique is related to the transient measurements of Bloembergen and Wang,[10] and was suggested by Hahn who also performed the earliest experiments.[11]

This research was undertaken to test the validity of the modified Bloch equations for large rf fields, and to determine the applicability of the technique in the study of paramagnetic substances in general.

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II. EXPERIMENTAL METHOD AND RESULTS

Preliminary measurements on diphenyl pycril hydrazil were made with a linearly polarized 21-Mc/sec rf field of up to 2 gauss peak amplitude, sinusoidally amplitude modulated at 0.5 Mc/sec. The signal was picked up by a 100-turn coil tuned to 0.5 Mc/sec and oriented along the z direction (fixed-field direction), and could be observed directly with a wide-band oscilloscope.

Under these conditions the predictions of the modified and unmodified Bloch equations are only slightly different from each other, and either could be made to fit the data equally well by assuming $T_1=T_2\cong 6.2\times 10^{-8}$ sec, in agreement with previous measurements. It was expected that the variations in M_z would lag behind the modulation envelope by a phase shift of about $\omega_m T_1$ radians, where $\omega_m/2\pi$ is the rf modulation frequency ($\frac{1}{2}$ Mc/sec). Unfortunately the system was not stable enough to resolve this phase shift.

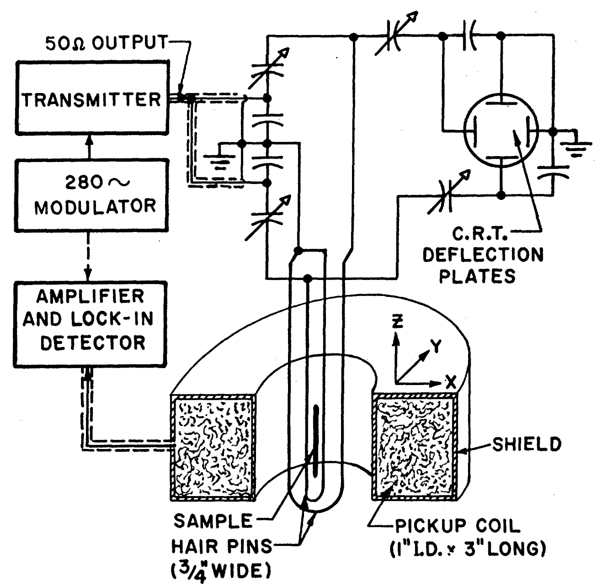

FIG. 1. Experimental apparatus. The coils used to produce the fixed field H_z are not shown.

Since the measurements with a linearly polarized rf field failed to give a sensitive test of the modified Bloch equations, we undertook to make a similar kind of measurement with a large circularly polarized rf field.

It was a simple matter to produce a circularly polarized field of up to 6 gauss at 19.5 Mc/sec by exciting two hairpins oriented at right angles, each one constituting the inductive leg of a tuned circuit (Fig. 1). In order to obtain equal amplitudes and a 90-degree phase difference, the two tank circuits had to be slightly detuned; this was done by trial and error. To check the amplitude and polarization of the rf field, the deflection plates of a cathode-ray tube were connected across the two hairpins through capacitive dividers. Care was taken to see that the phase and amplitude sensitivity of the cathode-ray tube was the same in both directions and that the two hairpins had the same dimensions. The two tank circuits were tuned to give a circle on the cathode-ray tube screen.

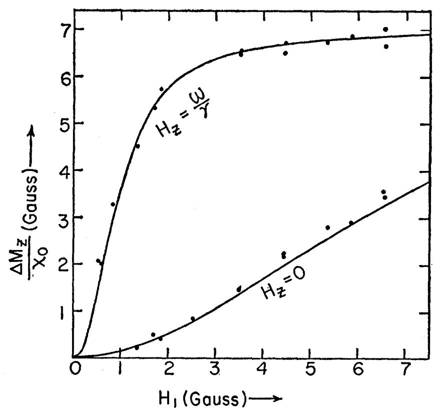

FIG. 2. Observed signal for zero dc field and resonant dc field, as a function of rf amplitude. The solid curves give the theoretical prediction of Eq. (3), assuming $T_1=T_2=6.2\times 10^{-8}$ sec, as measured previously.

The rf field was turned on and off at 280 times per second. Every time the transmitter turned on or off, there should be a change in M_z of

$$\Delta M_z=\pm(\chi_0 H_z-M_z)=\frac{\pm\chi_0\gamma\omega(H_1T_1)^2}{1+(\Delta\omega T_1)^2+(\gamma H_1T_1)^2}. \tag{3}$$

This change in magnetization produced voltage pulses

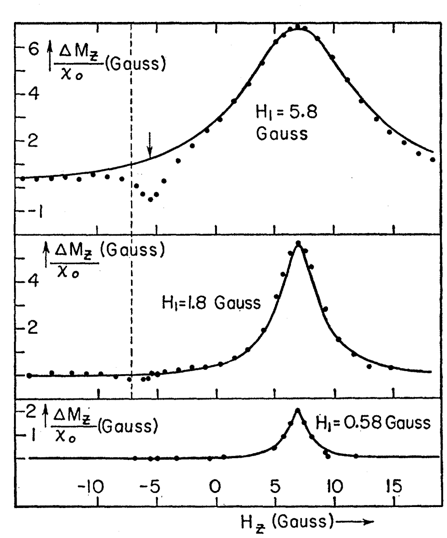

FIG. 3. Observed signal as a function of dc field, at various power levels. The solid curves give the theoretical prediction of Eq. (3) for pure circularly polarized rf field. The arrow on the upper curve is at the position of the negative peak predicted by Eq. (4), and the vertical dotted line shows the expected negative resonance condion ($H_z=-\omega/\gamma$) neglecting the Bloch-Siegert effect.

at 280 cps in a 30 000-turn pickup coil. The output of the pickup coil was fed into a high-gain narrow-band low-noise amplifier and lock-in detector, which had to be extensively shielded and rf bypassed. Since the rf field was turned on and off in a time short compared to the period of the rf modulation (1/280 sec), the output of the lock-in detector was proportional to ΔM_z.

In Fig. 2 are shown experimental data and theoretical curves for zero fixed field and for resonant fixed field. The detection system was not directly calibrated; instead, the gain of the system was taken to give the best fit at resonance ($H_z=\omega/\gamma$) in Fig. 2. The amplitude of the rf field was measured in three ways: with a search coil; by measuring the voltage across the hairpins; and by fitting the data at resonance with theory. The three calibrations thus obtained agreed within 10%. The calibration used here is the one chosen to give the best fit for the ($H_z=\omega/\gamma$) curve in Fig. 2. These two calibration constants were the only adjustable constants used to compare the experimental data with theory. The lower curve in Fig. 2 shows that there is a definite fixed magnetization when $H_z=0$, as predicted by the modified Bloch equations.

Figure 3 shows some typical runs at various rf levels. At high power level a small negative resonant peak is observed, which is due to the fact that the rf field is not perfectly circularly polarized, but contains about 10% oppositely rotating rf field (as inferred from the height of the negative resonance). This arises in part from imperfections in the production and measurement of the field, and in part from the fact that those parts of the sample which are off the central axis will not see a perfectly circularly polarized field even if everything is perfectly symmetrical. For this reason the sample was confined to a small radius.

The negative resonance peak is shifted from the condition $H_z=-\omega/\gamma$; this shift is similar to that predicted by Bloch and Siegert,[12] but in this case the shift can be calculated more exactly for large H_1. It can be shown, by transforming to a coordinate system rotating with the main part of the rf field, that the small negative peak due to the residual oppositely rotating rf field should occur when

$$\gamma H_z=\omega-(4\omega^2-\gamma^2 H_1^2)^{\frac{1}{2}}. \tag{4}$$

The position of the observed peak is in agreement with this prediction.

The data of Figs. 2 and 3 clearly contradict the unmodified Bloch equation but agree very well with the prediction (3) of the modified Bloch equations. The small discrepancies which are observed are probably spurious.

CONCLUDING REMARKS

The technique developed here may be useful for finding weak and broad paramagnetic resonances at low frequencies, because the signal is observed directly and not as a shift in the balance between two very much larger signals. Hence, with suitable design, it is possible to increase the rf amplitude considerably without increasing the detector noise. For those paramagnetic materials in which a resonance can be observed, the technique could also be used to measure spin susceptibility, and might be considerably simpler than other methods which depend on measurement of the strength of the paramagnetic resonance.[7,13]

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