## Spin-Lattice Relaxation and the Residual Width of Highly Exchange-Narrowed Paramagnetic Resonances*

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We have investigated the saturation properties of two highly exchange-narrowed paramagnetic resonances in low magnetic fields with a view to determining the contribution of the spin-lattice relaxation mechanisms to the line width. Both samples were polycrystalline free radicals: diphenyl picryl hydrazyl or DPPH, $(C_6H_5)_2N-N-C_6H_2(NO_2)_3$, and tris-*p*-nitro-phenyl methyl or TpNPM, $C(C_6H_4(NO_2))_3$. Our experiments indicate that the limitation which spin-lattice relaxation places upon the lifetime of the odd-electron spin state contributes much, if not all, of the line width at 60 Mc/sec.

At such low frequencies, rf magnetic fields as large as 1 oersted are readily obtainable. The rf spectrometer, a variation of that designed by Schuster,[1] was used in conjunction with a Watkins-Pound calibrator[2] to make saturation measurements.

A vacuum tube voltmeter was built into the apparatus to measure the rf voltage across the coil, from which the rf field was calculated as follows. The inductance of the sample coil, wound of small flat copper strap to minimize capacitance between turns, was determined at 60 Mc/sec. Next the ratio of magnetic field to current in the coil was obtained by performing an auxiliary resonance experiment in which the sample coil carried direct current and contributed to the constant external magnetic field for a still smaller rf coil containing a free radical. The result is that $H_1=0.022V$, where $V$ is the rms voltage at 60 Mc/sec and $H_1$ is the half-amplitude of the rf field, in oersteds, at the center of the coil. To the extent that the current distribution in the coil is not the same at 60 Mc/sec as for dc, this calibration may introduce some systematic error.

In the absence of a rigorous quantum treatment of the line profile as influenced by spin-lattice relaxation, dipolar spin-spin interactions, exchange, and the rf field amplitude, we use the phenomenological equations of Bloch[3] in the light of their justification from a microscopic viewpoint by Wangsness and Bloch.[4] That justification neglects spin-spin interaction and may at first seem inapplicable when both exchange and dipolar spin-spin interactions are present. However, exchange[5,6] tends to render incoherent the dipolar interactions. If this effect is pronounced, Wangsness and Bloch's analysis can apply, along with the result $T_2=T_1$ obtained for their case *d*, "isotropic molecular surroundings." The characteristic frequency $\omega^*$ of Wangsness and Bloch is then essentially the $\omega_e$ of reference 6.

The imaginary part of the Bloch susceptibility[7] is, when $T_2=T_1$,

$$\chi''=\tfrac{1}{2}\chi_0\omega_0T_1\frac{1}{1+T_1^2(\omega-\omega_0)^2+\gamma^2H_1^2T_1^2}. \qquad (1)$$

Equation (1) describes a line profile of the Lorentz or damped-oscillator shape, which fits our experimental line shapes excellently and is in agreement with expectations based upon theory and other experiments.[6] The half-width $\Delta\omega_{\frac{1}{2}}$ at half-maximum intensity obtained from Eq. (1) is

$$\Delta\omega_{\frac{1}{2}}=[T_1^{-2}+\gamma^2H_1^2]^{\frac{1}{2}}. \qquad (2)$$

The calibrator, which was used with a field-modulation apparatus sensitive to the derivative of the line shape, measures the saturation factor $S'=[d\chi''(H_1)/d\omega]_{\max}/[d\chi''(0)/d\omega]_{\max}$ which is, from Eq. (1),

$$S'=[1+\gamma^2H_1^2T_1^2]^{-\frac{3}{2}}. \qquad (3)$$

Figure 1 compares a curve of $S'$ *versus* $V$ for $T_1=6.3\times10^{-8}$ sec with experimental values of $S'$ for DPPH; the experimental half-width $\gamma^{-1}\Delta\omega_{\frac{1}{2}}$ is also plotted. The validity of the assumption that $T_2=T_1$ is tested by comparing $(\gamma T_1)^{-1}=0.90$ oersted with $\gamma^{-1}\Delta\omega_{\frac{1}{2}}=0.97\pm0.05$ oersted at low rf voltage.

Similarly $T_1=1.6\times10^{-7}$ sec fits the data for TpNPM, and $(\gamma T_1)^{-1}=0.35$ oersted is to be compared with $\gamma^{-1}\Delta\omega_{\frac{1}{2}}=0.36\pm0.03$ oersted at low rf voltages.

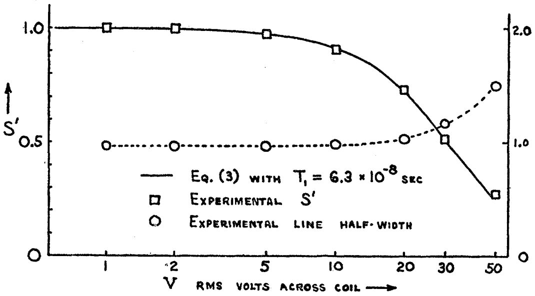


FIG. 1. Comparison of calculated and experimental values of the saturation factor $S^1$ a sa function of the rms voltage $V$. The experimental half-width $\gamma^{-1}\Delta\omega_{\frac{1}{2}}$ is also plotted as a function of $V$.

These measurements indicate directly that the spin-lattice relaxation time $T_1$ contributes much or all of the line width in DPPH or TpNPM. In general, $T_1$ should depend upon the external magnetic field,[8] and one should not expect the widths of these highly exchange-narrowed resonances to be independent of the resonant frequency. Indeed, $0.97\pm0.05$ oersted for the DPPH half-width at 60 Mc/sec is to be contrasted with $1.35\pm0.05$ oersteds obtained by Professor J. Townsend of this laboratory at about 9000 Mc/sec and $1.36\pm0.01$ oersteds obtained at a similar microwave frequency by Professor R. T. Weidner at Rutgers University.[9] It should be noted, however, that this indicated decrease of $T_1$ with increasing field runs counter to the prediction of theory for the so-called Raman processes treated by Van Vleck.

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## Spontaneous Hall Effect in Ferromagnetics

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The Hall voltage in ferromagnetics[1] at saturation can be expressed in the form:

$$E_y/i_x=\rho_{yx}=-\rho_{xy}=A_H\cdot B_z+\rho_{SH}. \qquad (1)$$

$A_H$ is the normal Hall coefficient and $\rho_{SH}$ the spontaneous Hall resistivity. We have measured the Hall effect of several specimens of nickel and a number of its alloys in fields up to 14 000 gauss and, in addition, their resistivity $\rho$. The results are given in Table I. All samples have been annealed for 1 hr at 1000°C in pure $H_2$.

For our Ni sample with smallest residual resistivity, $\rho_{SH}$ vanishes at low temperatures.[2] For alloys, however, $\rho_{SH}$ remains finite, and, in general, $\rho_{SH}$ varies roughly in the same way as $\rho$. Mostly the spontaneous Hall angle is $\frac{1}{2}$ or $1\times10^{-2}$.

Three possible causes for the spontaneous Hall voltage are

(a) internal real magnetic fields resulting from the dipoles,
(b) spin-orbit interaction,[3,1]
(c) the inhomogeneous magnetic field induced by the primary current $i_x$.[4,1]