NEW EFFECT IN DYNAMIC POLARIZATION*

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(Received 15 December 1966)

A new effect in dynamic polarization is found showing characteristics similar to those of the "solid effect" but with significant difference in the spacing between enhancement peaks. A possible explanation, ascribing it to the electron spin-spin interaction, is discussed.

In the theory of dynamic polarization of nuclei by the "solid effect,"[1,2] the spacing (D) between the positive and negative nuclear-polarization enhancement peaks ($\pm E_{\mathrm{max}}$) is a well-defined quantity for a system with completely resolved forbidden transitions. For systems in which both the electronic and nuclear spins are $\frac{1}{2}$, one has $D = 2\omega_n$, where ω_n is the nuclear Larmor frequency at a given static magnetic field (H_0) This relationship has been verified by Jeffries and Schmugge[3] in their experiments on a lanthanum magnesium double nitrate crystal doped with nominally 1% Nd^{142} (Nd-LMN). Jeffries also showed[1] that $2\omega_n$ represents a minimum value of D, and that D may generally be larger due to the broadening of the epr line and to oversaturation.

We found D to be appreciably less than $2\omega_n$ in the dynamic polarization of protons in chemically doped polystyrene or toluene at 4.2°K and a microwave pumping frequency (ω) of 70 GHz. The methods of sample preparation and polarization measurement are described elsewhere.[4] The doping free radicals used and their respective epr full widths at half-maximum ($\Delta H_{1/2}$), measured at 9 GHz in dilute form in polystyrene, are diphenyl-picryl-hydrazyl (DPPH), $\Delta H_{1/2} = 36$ G; Coppinger's radical[5,6] (galvinoxyl), $\Delta H_{1/2} = 16$ G; and Ley's radical,[6,7] $\Delta H_{1/2} = 9$ G. Figure 1 shows some typical proton dynamic polarization enhancements (E) as a function of H_0 at constant ω and microwave power level ($\overline{W}$). Curve a illustrates the pure "solid effect" in Nd-LMN. Curve b shows that E for a sample of 0.25% Ley's radical (by weight) in polystyrene exhibits qualitatively the pure "solid effect" behavior, with $D \approx 2\omega_n$. With increasing radical concentration we found $D \approx 1.3\omega_n$ as shown in curves c and d.

The same spacing, $D \approx 1.3\omega_n$, and curves of E vs H_0 similar in shape to that of Fig. 1(d) were also observed for 5% Ley's radical in frozen toluene at 4.2°K and for 5% galvinoxyl in polystyrene at 4.2 and 1.2°K. A reduced D is not limited to these two radicals since we also observed $D \approx 1.5\omega_n$ for 3.3% DPPH in polystyrene at 4.2°K. The absolute value of H_0 was monitored continuously during the experiment by a F^{19} nmr spectrometer with the F^{19} probe located outside the multimode microwave cavity. In addition, both ω and ω_n were also monitored, and we found $\omega \approx g_e \beta H_0$ and $\omega_n = g_n \beta_n H_0$ with H_0 given by the F^{19} nmr spectrometer. Hence we believe that the error in D due to uncertainties in H_0 was negligible.

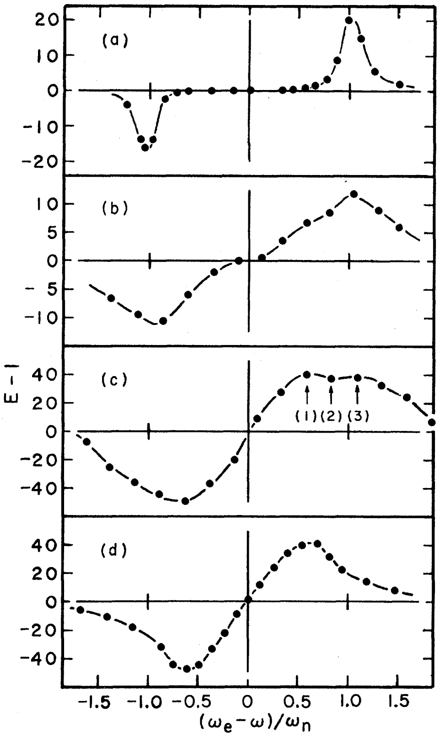

FIG. 1. Free-proton dynamic-polarization enhancement versus static applied magnetic field at 4.2°K and 70 GHz. (a) 1% Nd^{142} in LMN; (b), (c), and (d) 0.25, 1.5, and 5% Ley's radical by weight in polystyrene, respectively. In (a), the central value of H_0 is 18.7 kG ($g_e \approx 2.7$); in (b)-(d) the central value is 25.0 kG ($g_e \approx 2.0$). The microwave power expended in the cavity (volume $\approx$ 12 cm^3) was about 25 mW in all cases, and no power extrapolations of the measured enhancements were made.

One possible cause of this reduced D is an apparent shift of the g factor of the electrons due to the local-field contribution of the polarized protons. However, if this is so, then the magnitude of the local-field contribution, and consequently the magnitude of D, must necessarily depend upon the degree of absolute proton polarization. We have measured the value of D for 5% galvinoxyl in polystyrene at 4.2 and 1.2°K at a constant $\overline{W}_{\mathrm{max}}$ as well as at reduced $\overline{W}$ (15 dB down from $\overline{W}_{\mathrm{max}}$) at 4.2°K. These conditions corresponded to a variation of absolute proton polarization from 0.6 to 17%, yet D remained constant under all these conditions. Therefore we can safely rule out the hypothesis of local-field contribution due to the polarized protons.

The case of 1.5% Ley's radical in polystyrene [see Fig. 1(c)] is particularly interesting because the results showed two almost-resolved peaks in the $+E$ side of the curve of E vs H_0. We interpret this to be an indication of the simultaneous existence of an $E_{1\mathrm{max}}$ due to the pure "solid effect" and an $E_{2\mathrm{max}}$ due to the new effect in a sample of given radical concentration. Moreover, when curve c in Fig. 1 is considered together with curves b and d, the trend of variation suggests a transition from the dominance of a pure "solid effect" at lower radical concentrations to the dominance of a new and distinct effect at higher concentrations. The interpretation is reinforced by the radically different dependences of E on $\overline{W}$ at three positions near the two "peaks," as shown in Fig. 2.

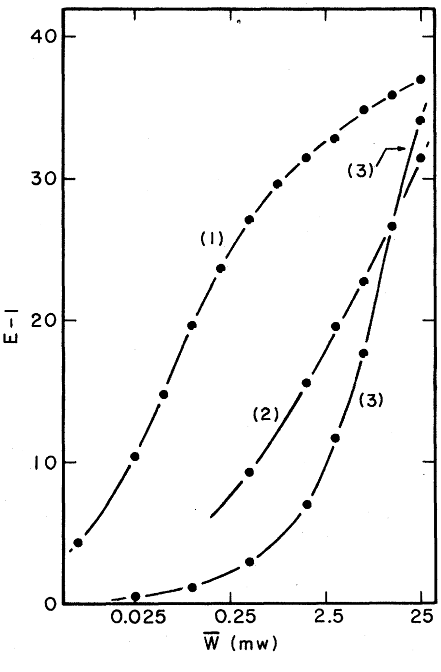

FIG. 2. Free-proton dynamic-polarization enhancement versus applied microwave power at the applied magnetic fields corresponding to the points (1), (2), and (3) of Fig. 1(c).

Since this new effect gives both positive and negative E, unless there exists some mysterious mechanism by which the electron-proton coupling would change from scalar to dipolar from one side of the epr to the other, this new effect cannot be a simple classical Overhauser or "underhauser" effect. We have tried to account for this new effect by invoking a classical Overhauser effect in conjunction with induced electron-proton cross relaxation due to the presence of the excited forbidden transitions. However, such a mechanism would give an E of the opposite sign from that observed, and this was verified by a rate equation calculation.

Abragam and Borghini[2] used a Hamiltonian in a rotating frame and calculated the nuclear spin temperature for a two-spin system at arbitrary rf field strength using a density-matrix approach. This Hamiltonian was of the form

$$\mathcal{H}^* = (\omega_e - \omega)\sum_i S_{iz} + \omega_n \sum_j I_{jz} + H_{ss}^{\;0}$$
$$= \mathcal{L}^* + M^* + H_{ss}^{\;0}, \qquad (1)$$

where $\mathcal{L}^*$, M^*, and $H_{ss}^{\;0}$ are, respectively, the electronic Zeeman energy, the nuclear Zeeman energy, and the secular part of the electron spin-spin interaction energy; ω_e is the electronic Larmor frequency. Their results showed that in addition to the nuclear polarization due to the pure "solid effect," there might be a "heretofore unobserved" nuclear-polarization effect due to the spin-spin interaction among the electrons (hereafter called spin-spin effect). Although their calculations were carried out in the high-temperature approximation whereas our measurements were made at low temperatures, their calculated nuclear polization due to the spin-spin effect showed qualitative features consistent with the observed characteristics of this new effect. In particular, their results predicted that $\pm E_{\mathrm{max}}$ due to the spin-spin effect might be closer to the center of the epr than those due to the pure "solid effect," and that in the high-power limit the curve of E vs H_0 for the spin-spin effect should have the shape of a dispersion curve in contradistinction with the resolved structure for a pure "solid effect."

We have extended the Abragam-Borghini calculations by including second- and third-order spin-temperature terms in the density matrix and the expectation values of the various terms in the Hamiltonian. Using the notation developed by Abragam-Borghini,[2] we find that because $\mathrm{Tr}(H_{SS}{}^0)=0$, as assumed by these authors, the quantities $\partial\langle\mathcal{L}^*\rangle/\partial\alpha$, $\partial\langle M^*\rangle/\partial\beta$, $\partial\langle H_{SS}{}^0\rangle/\partial\gamma$ are in the form $1+X_r(\alpha,\beta,\gamma)$ where r refers to $\mathcal{L}^*$, M^*, or $H_{SS}{}^0$, and X_r contains only terms quadratic in spin temperatures. Consequently these quantities do not contribute any new real solutions of spin temperature to the following rate equation:

$$\left[\left(\frac{\partial}{\partial t}\right)_L+\left(\frac{\partial}{\partial t}\right)_{H_1}\right]A=\left(\frac{\partial}{\partial \xi}A\right)\left[\left(\frac{\partial}{\partial t}\right)_L+\left(\frac{\partial}{\partial t}\right)_{H_1}\right]\xi=0, \quad (2)$$

where A is $\langle\mathcal{L}^*\rangle$, $\langle M^*\rangle$, or $\langle H_{SS}{}^0\rangle$ as previously defined and ξ is the relevant spin temperature α, β, or γ. The time derivatives $(\partial/\partial t)_L$ and $(\partial/\partial t)_{H_1}$ refer, respectively, to change due to relaxation process and induced transitions, and our higher order calculations give exactly the same expressions for real α, β, and γ as those calculated by Eqs. (21) and (22) in Ref. 2. Hence we can take their Eq. (23) to be the expression for the nuclear spin temperature in our approximation also. To explore the low-temperature approximation further, one should probably examine the possibility of including higher order spin-temperature terms in the time derivative of the spin temperature in Eq. (2).

Although the Abragam-Borghini spin-spin effect exhibits qualitatively the features of the new effect reported here, there are several puzzling aspects which remain unresolved. First of all, from the concentration dependence of the new effect, we are forced by Eq. (23) of Ref. 2 to conclude that the quantity $\omega_L{}^2$ defined by these authors as $\mathrm{Tr}(H_{SS}{}^0)^2/\mathrm{Tr}(S_z)^2$ must increase as the radical concentration decreases, but one would expect the opposite to be true from the definition of $\omega_L{}^2$. Secondly, Scott[8] has indicated that the epr linewidths of these organic free radicals in an amorphous host remain constant independent of H_0. If this is indeed true, then our 3-kG epr measurements suggest that neither the allowed nor the forbidden transitions would be very strongly excited at the observed positions of $\pm E_{\max}$ due to this new effect. Thirdly, Abragam and Borghini[2] point out that $\pm E_{\max}$ for the spin-spin effect should occur at $\omega_e-\omega\approx\sqrt{2}\omega_L$. Since their Eq. (23) dictates that in the high-power limit we must have $\omega_L\leq 0.1\omega_n$ in order to account for the observed relative strength of $E_{1\max}$ and $E_{2\max}$, this would give a value of $D\lesssim 0.3\omega_n$ which is considerably smaller than the $D\approx 1.3\omega_n$ observed. Further theoretical and experimental studies would be necessary to fully understand this new effect.

We wish to thank D. S. Schreiber for many interesting discussions, Shigeki Suwa for the Nd-LMN crystal, and Bruce A. Hasher for his general assistance.

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*Work supported in part by Advanced Research Projects Agency and a Northwestern University Institutional Grant.

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