DYNAMIC POLARIZATION ANOMALIES IN ORGANIC FREE RADICALS*

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As a part of a broader study of exchange effects in various paramagnetic substances, we have found an organic free radical in which the Overhauser effect gives way to a "solid" effect at low temperature, and one in which the two effects are present simultaneously.

The Overhauser effect[1] is produced by saturation of the electron spin resonance (ESR) transition in a system in which the nuclei are coupled to the electrons by a hyperfine interaction. It appears as an enhancement of the nuclear polarization, and therefore of the nuclear magnetic resonance (NMR) signal. The "solid" effect,[2] on the other hand, depends on dipole-dipole coupling between the electrons and nuclei in a solid and requires the saturation of the forbidden transitions at $\nu = (|\gamma_e| \pm \gamma_n)H_0$, where ν is the microwave frequency and γ_e and γ_n are the electronic and nuclear gyromagnetic ratios. H_0 is the external (dc) magnetic field. These forbidden transitions involve simultaneous flips of a nucleus and an electron. Saturation of the transition at $(|\gamma_e| + \gamma_n)H_0$ results in a negative enhancement of the NMR signal (the nuclear polarization is inverted), while that at $(|\gamma_e| - \gamma_n) \times H_0$ produces a positive enhancement. Typically, the forbidden transitions are more easily saturated than the allowed ones, so that much less saturating power is necessary to produce the solid effect than the Overhauser effect, if it is present.

The Overhauser effect in the organic free radical diphenyl picryl hydrazyl (DPPH) is relatively well known.[3] The enhancement obtained at 3400 oersteds is, however, small (about 20) at room temperature and at 77°K. It disappears in the liquid helium temperature range, being masked by a collapsing of the Knight shift and by microwave heating effects.[4]

Wurster's blue perchlorate (WB) has an exchange-narrowed electron spin resonance about 3 oersteds wide at room temperature.[5] At 300°K and at 77°K it gives only an Overhauser effect (Fig. 1). In the liquid helium range, it exhibits only a solid effect (Fig. 1). Here the ESR line is 14 oersteds wide and the proton NMR 14 oersteds, giving rise to an effective broadening of the solid effect spectrum. Power dependence of the two effects is shown in Fig. 2, which is typical of Overhauser effects in all the free radicals, and of solid effects in general.

Picryl amino carbazyl (PAC) resembles the other free radicals in its electron spectrum at room temperature.[6] It has one of the larger g-factor anisotropies among the organic free radicals. It exhibits both solid and Overhauser effects at 300°K and 77°K, with a pure solid effect at 4.2°K and below (Fig. 3).

These two free radicals differ from DPPH in the temperature dependence of their susceptibilities (see Fig. 2 of Rhodes et al.[7]). They also are known to show $g=4$ satellite[7] lines below a

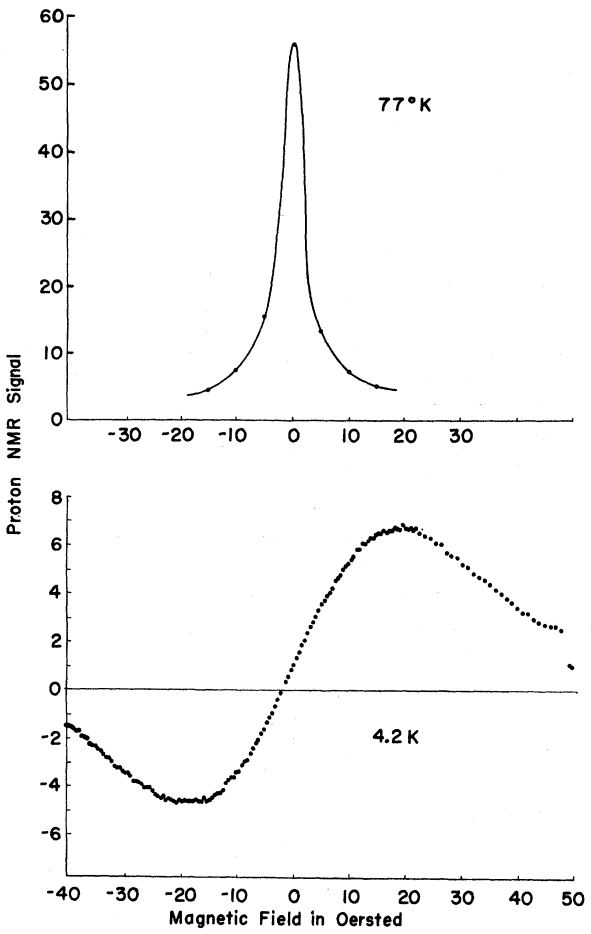

FIG. 1. Proton NMR signal in arbitrary units as a function of magnetic field in Wurster's blue. The microwave frequency is held constant at 9.7 kMc/sec. ESR occurs at $H_0 = 0$.

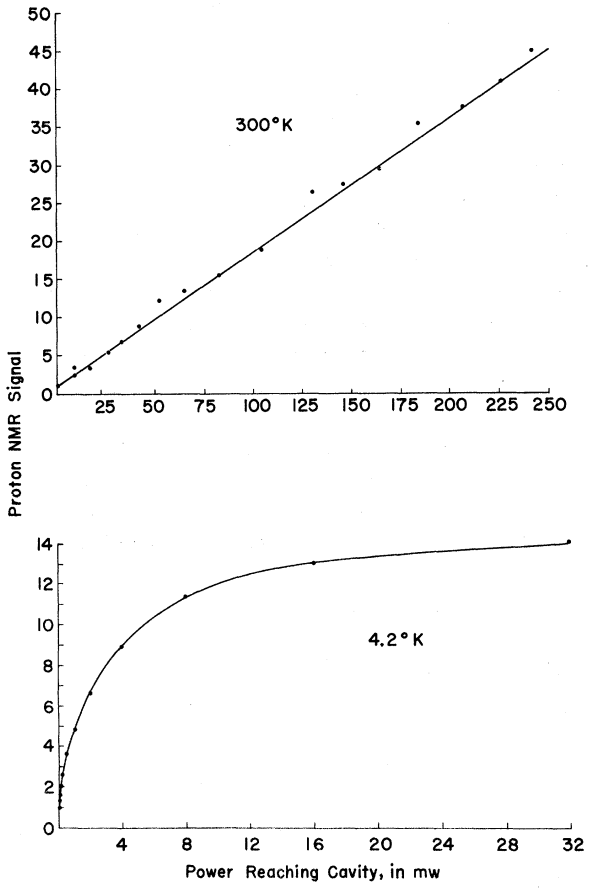

FIG. 2. Proton NMR signal in arbitrary units as a function of saturating power, at the peak of the enhancements in WB.

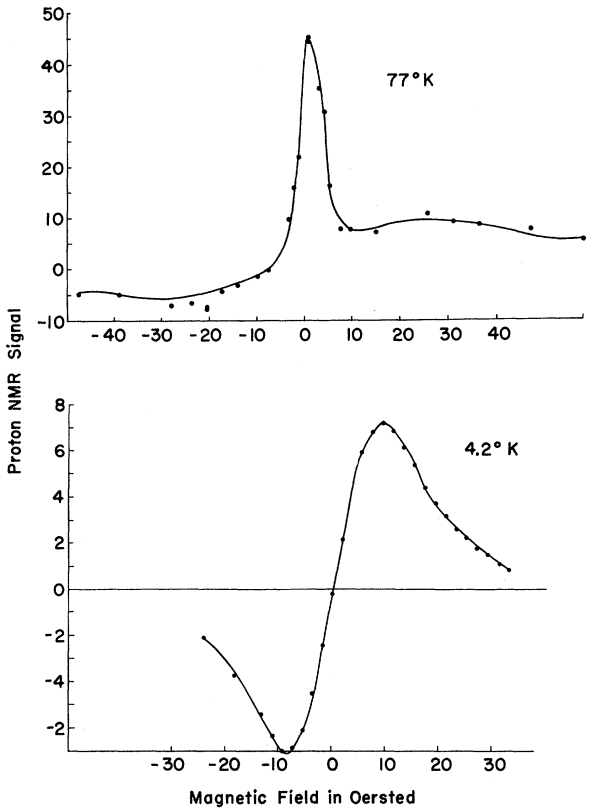

FIG. 3. Proton NMR signal in arbitrary units as a function of magnetic field in PAC. The microwave frequency is held constant at 9.7 kMc/sec. ESR occurs at $H_0 = 0$.

characteristic temperature T^* which is higher in WB. The transition between the two types of dynamic polarization which we observe comes above T^* in PAC, below it in WB. However, the existence of the $g=4$ lines is apparently due to the presence of dipolar coupling, which is in turn related to the decrease in susceptibility and its consequent effective magnetic dilution. It is this effective magnetic dilution which we suggest may provide the nuclear-electron dipolar coupling which gives rise to the solid effect. It does not follow that the transition temperature for the nuclear-electron effects need be the same as that for the purely electronic phenomenon. Support for this is provided by a fourth free radical, 1-3-bis-diphenylene-2-phenyl allyl (BDPA) which shows a $g=4$ line below 2°K,[7] but retains a reduced proton Knight shift[8] at this temperature—showing that the proton-electron coupling is still primarily scalar (hyperfine). No solid effect has been observed in this substance at the lowest temperatures so far employed (about 1.8°K), and we have some evidence of a residual Overhauser effect at 4.2°K.

We are continuing our investigations of these materials in an effort to understand the nature of the susceptibility anomalies and the influence of exchange on the interactions among electrons and between electrons and nuclei in solids.[9]

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[1]A. W. Overhauser, Phys. Rev. 92, 411 (1953). For further references see R. H. Webb, Am. J.

Phys. (to be published).
[2]A. Abragam and W. G. Proctor, Compt. rend. 246, 2253 (1958). For further references see R. H. Webb, Am. J. Phys. (to be published).
[3]H. G. Beljers, L. van der Kint, and J. S. van Wieringen, Phys. Rev. 95, 1683 (1954).
[4]R. H. Webb (to be published).
[5]S. I. Weissman, J. Townsend, D. E. Paul, and G. E. Pake, J. Chem. Phys. 21, 2227 (1953).
[6]C. Kikuchi and V. W. Cohen, Phys. Rev. 93, 394 (1954).
[7]R. S. Rhodes, J. H. Burgess, and A. S. Edelstein, Phys. Rev. Letters 6, 462 (1961).
[8]M. E. Anderson (to be published).
[9]Note added in proof. The solid effect in BDPA has now been seen at 1.4°K.

THERMAL CONDUCTIVITY OF NORMAL AND SUPERCONDUCTING LEAD ALLOYS*

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The thermal conductivity of lead specimens containing 3% indium, 6% indium, and 6% bismuth has been measured in the normal and superconducting states. The data are shown in Fig. 1. Their analysis shows that the addition of impurity leads to an increase in thermal resistance in both states, but that near 2°K the ratio of increase in the resistance to lattice heat transport is 40 times greater in the normal state than in the superconducting state. Since in superconducting lead, at 2°K and below, the electronic conductivity and the effect of the electrons on the lattice conductivity are expected to be negligible, it is seen that the large change in lattice thermal resistance with impurity in the normal state depends on the presence of the electrons.

In the normal state the electronic thermal conductivity is equal to αT, where the coefficient α is related to the residual electrical resistivity ρ_0 by the Wiedemann-Franz law, $\alpha = L_0/\rho_0$ ($L_0 = 2.445\times10^{-8}$ volt^2/deg^2).[1] At sufficiently low temperatures the lattice conductivity is equal to βT^2. The total thermal conductivity $K = \alpha T + \beta T^2$ is most easily separated into its components graphically, on a plot of K/T versus T which will then be a straight line. In Fig. 2 the experimental data for the normal state have been plotted on such a graph. For each specimen the intercept α has been calculated from a measurement of the electrical resistance near 4.2°K, and a straight line drawn through this point and through the low-temperature thermal conductivity points. The slope β of each line is shown in Table I. In addition Table I lists the values of ρ_0 for our specimens and of β and ρ_0 for a specimen of lead with 0.7% bismuth measured by Montgomery.[2] The deviation of the data from the straight lines at higher temperatures is likely to be caused by the increased importance of impurity scattering at these temperatures.

The effect of adding impurity may be calculated roughly by comparing the thermal resistances of specimens containing different amounts of impurity. The lattice resistances at 2°K are

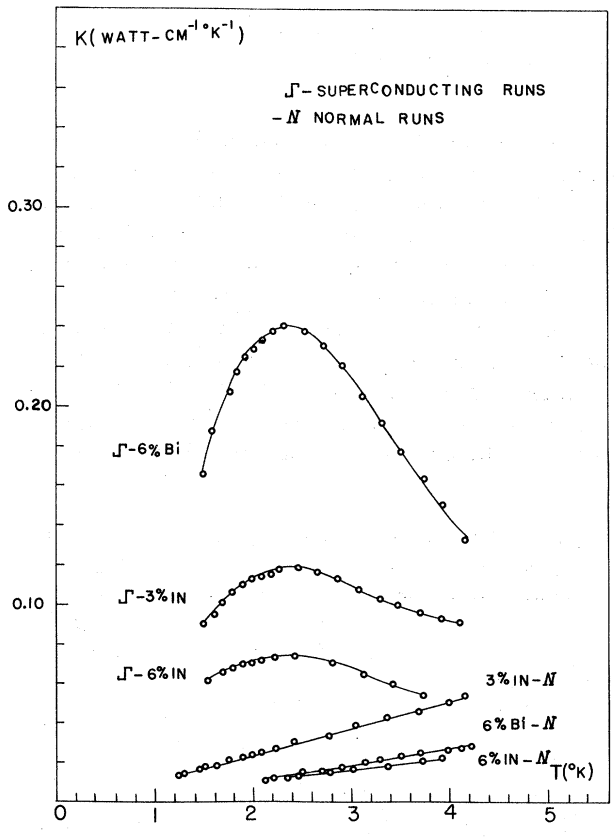

FIG. 1. Thermal conductivity of lead alloys versus temperature.