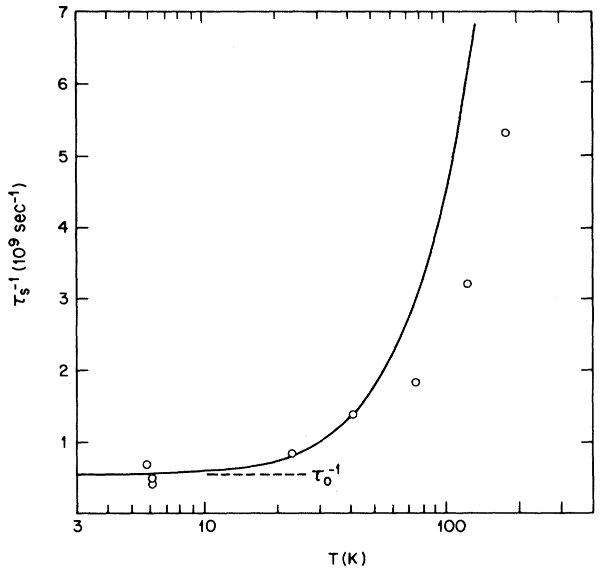

FIG. 2. Electron-spin–relaxation time as a function of temperature for a zinc concentration 4.5×10^{18} cm^{-3}. Curve is the theoretical fit (19) with one adjustable parameter $\tau_0 = 1.8\times10^{-9}$ s.

over the range (5×10^{17}–2×10^{19} cm^{-3}) at $T = 6$ K. The very slow variation with N_A is characteristic of electron relaxation by collisions with a degenerate hole population. Figure 2 shows τ_s vs T for $N_A = 4.5\times10^{18}$ cm^{-3}. The finite lower limit at low temperatures is characteristic of the H_T mechanism. The curve in Fig. 2 is a fit of the form

$$\tau_s^{-1} = \tau_s^{-1}(H_T) + \tau_s^{-1}(H_L) \tag{19}$$

by using one adjustable parameter $\tau_0^{-1} = 5.5\times10^8$ s^{-1}.

The experimental value of τ_0^{-1} is less than the theoretical value (15), which is in the direction to be expected[2] for the effect of hole-impurity scattering, hole-hole scattering, and the spin-nonflip part of the electron-hole scattering, all neglected in our model. In view of these comments, we regard the agreement with experiment as satisfactory and emphasize that of all the known spin relaxation mechanisms, only the H_T process even qualitatively accounts for the low-temperature data for the degenerate case.

The inspiration to consider the virtual-photon (H_T) mechansim came to us from reading an unpublished memorandom by Morgan and Kane.[10] We thank R. A. Logan for the excellent epilayer materials from which our samples were made.

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Diffusion of Methyl-Group Tunneling Energy

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Dynamic nuclear polarization is observed when methyl groups in ammonium acetate at 4.2 K are converted between E and A spin-symmetry species by paramagnetic impurities whose Zeeman splitting is tuned to the methyl-group tunnel splitting. Further nuclear polarization is subsequently generated as the effect on resonant methyl groups is transferred to nonresonant ones by spin-symmetry diffusion. The time constant for the establishment of internal thermal equilibrium among the methyl groups is measured.

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The tunnel splitting between the ground torsional states of the A and E proton-spin–symmetry species of hindered methyl groups in solids at low temperatures gives rise to phenomena similar to those exhibited by spin-$\frac{1}{2}$ systems. In this paper we describe the first clear observation of spin-symmetry diffusion (SSD) and the first measurement of its rate. SSD is the analog of spin diffusion[1] in which rotational energy passes from one methyl group to another, leading not only to spatial diffusion of energy but also to spectral diffusion throughout a spectrum of tunnel splittings. SSD occurs because of a methyl-group flip-flop process, in which one methyl group is converted from E to A symmetry, while a second group makes the reverse transition. The combined process conserves energy except for a small difference in the two tunnel splittings. This small energy mismatch can be made up by a flip of a proton spin in the external magnetic field, with the result that SSD is accompanied by a dynamic polarization of the protons. This provides a means for its study with use of pulsed nuclear magnetic resonance (NMR) to measure the polarization.

The tunnel splitting $\hbar\omega_t$ is associated with quantum-mechanical reorientation of the group through the hindering barrier and is a sensitive function of the barrier height. Some dispersion of the tunnel splitting is expected, either due to mechanical coupling between groups[2] or due to random lattice strains, and this dispersion tends to inhibit diffusion,[3] the flip-flop matrix elements being small. SSD is caused by EE terms in the symmetry-adapted inter-methyl-group proton dipole-dipole interactions. (A and E label the irreducible representations of the group of cyclic permutations of the three protons of one methyl group.) These depend on the intergroup distance r approximately as r^{-5}, so that only flip-flops involving near neighbors need be considered. Other indirect mechanisms arise in higher orders of perturbation theory through the coupling of both groups to other spins.

The experiments which we report exploit the tunnel resonance method.[4-9] The idea is to tune the Zeeman splitting of unpaired electron spins (free radicals formed by γ irradiation of the sample), present as a dilute impurity, to the tunnel splitting of neighbor methyl groups. At the resonant magnetic field, energy is transferred between electron and methyl groups, the electron spin causing spin-symmetry conversion of the methyl groups through the E part of the electron–methyl-group dipole-dipole interaction.[10] As a by-product of this process, proton dynamic polarization occurs and is detected by NMR. In previous experiments[5-9] of this kind on MDBP (4-methyl-2,6-ditertiarybutylphenol) it was possible to account for almost all the results by assuming that SSD did not occur.

Each unpaired electron spin (free radical) is surrounded by a sea of methyl groups which are hot because the populations of E and A levels are unable to follow the lattice temperature when this is reduced to 4 K since the normal conversion rate is very slow. When the magnetic field is set near the tunnel resonance, the electron provides a cross-relaxation path by means of which neighbor resonant methyl groups can cool. This cross-relaxation process is due to terms like S_+I_z, S_+I_+, and S_+I_- in the electron–methyl-group dipole-dipole interaction which are resonant for $\omega_s=\omega_t$, $\omega_s-\omega_p=\omega_t$, and $\omega_s+\omega_p=\omega_t$, respectively, where ω_s and ω_p are the electron and proton Larmor frequencies. Transitions due to S_+I_+ and S_+I_- cause proton polarization in opposite senses. The electron thus cools three sets of neighbor methyl groups having values of ω_t satisfying the above conditions. Since the rate of cooling depends on the distance of the methyl group from the electron, one visualizes a bubble of coldness slowly growing around the electron, but, in the absence of SSD, only affecting resonant groups. Changing the magnetic field brings other methyl groups into resonance with the electron, and initiates the growth of a new bubble of coldness. The state of the assembly of methyl groups is described statistically[7] by a spin-symmetry temperature function in four dimensions, varying with the position of a methyl group relative to the nearest electron, and also with the tunnel splitting of the methyl group. This temperature function evolves according to the sequence of the magnetic-field changes and determines the rate at which nuclear polarization is generated. Thus the experiments described by this model exhibit a startling hysteresis which was an outstanding feature of the results on MDBP.[6-9]

The introduction of SSD into this model has two main consequences. The temperature function evolves continuously towards an internal thermodynamic equilibrium due to spectral and spatial diffusion, and hence diminishing hysteresis; this process is detected directly by the associated nuclear polarization. The clearest evidence for the absence of SSD in MDBP occurred in "hole-drilling" experiments.[6,7] Methyl groups having a particular value of tunnel splitting $\hbar\omega_0$ were cooled by contact with the electron (we neglect the small difference between ω_0 and $\omega_0\pm\omega_p$) and then the sample was left in a nonresonant magnetic field for several hours before an experiment was made to inspect the spin-symmetry temperature function, to see whether the cooled groups had exchanged energy with those which had not been cooled. In this inspection the hot groups generate nuclear polarization when $\omega_s = \omega_t$ while the cold ones do not. As a function of ω_s, the polarization traces out a bell-shaped curve reflecting the distribution of ω_t about its mean value, ω_m, but at $\omega_s = \omega_0$ a deep hole appeared, confirming that no significant exchange of energy had occurred, and that the tunnel-splitting distribution was inhomogeneously broadened.

Ammonium acetate was chosen for the present study because its tunnel splitting had already been measured by high-resolution inelastic neutron scattering[11] and because it is possible to generate stable free radicals in acetates by irradiation at room temperature.[12] The proton magnetization was measured by observing the amplitude of the free induction decay following a 90° pulse. A field-cycling technique was used which allowed all measurements to be made at a field of 0.3476 T (NMR frequency = 14.8 MHz). The sequence was as follows: (a) With the field at 0.3476 T. the magnetization was reduced to zero by a series of rf pulses; (b) the field was switched in a time of about 5 sec to a chosen value where it remained for 110 sec; (c) the field was returned to 0.3476 T and the nuclear magnetization measured. This sequence was repeated for many values of the field in step (b). Figure 1 shows how the magnetization measured in step (c) depends on the field used in step (b). The hole-drilling experiment is quite similar except that there is a preliminary step in which the magnetic field is set so that $\omega_s = \omega_0$ for a relatively long period.

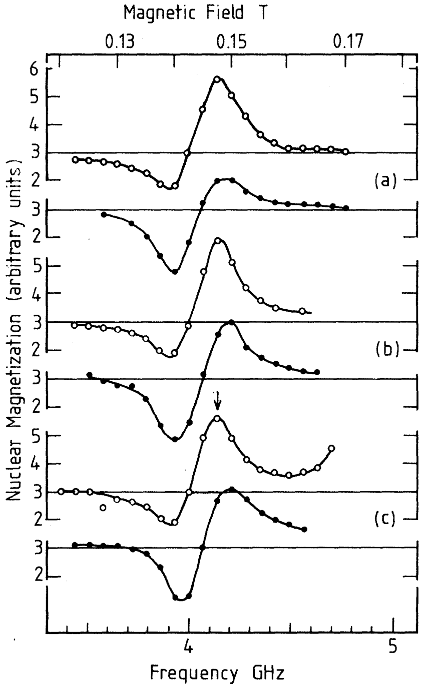

FIG. 1. Nuclear magnetization recovery of irradiated ammonium acetate at 4.2 K, taken with magnetic field decreasing (open circles) and increasing. (a), (b), and (c) are first, second, and fourth double passes through the resonance, respectively. A hole-drilling interlude was introduced between the third and fourth passes, with the field at the arrowed position in (c). The hole heals within a few minutes, affecting the first few measurements on the right of upper trace (c).

Figure 1 shows a succession of measurements at 4 K, made first with the field reducing (open circles) and then increasing, with (a), (b), and (c) denoting the first, second, and fourth double passages through the resonance, respectively. Between the third and fourth passages, a hole-drilling step was introduced, the magnetic field being set to 0.1475 T ($\omega_0/2\pi = 4.13$ GHz) for a period of 20 min. In contrast with MDBP (Ref. 6), no hole was found (at the position of the arrow) in Fig. 1(c). The healing of the hole shows up, though, in the next few measurements made at the high-field end of the upper curve of Fig. 1(c). The observed magnetization is the sum of the effects of relaxation and dynamic polarization.

Figure 2 shows direct measurements of the rate of approach to internal equilibrium. The field was first set to 0.1475 T (open circles) for a period of 110 sec. Then the field was switched to 0.3476 T and the magnetization recovering in a time of 45 sec was measured at intervals of 54 sec, the magnetization being reduced to zero after each measurement. The approach to a steady signal with a time constant of about 5 min reflects the healing of the hole. The nonresonant electron plays no role in the dynamic polarization. The closed cir-

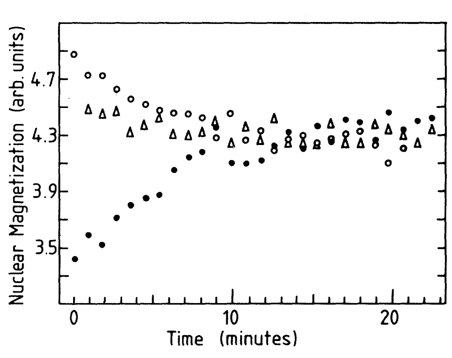

FIG. 2. Nuclear magnetization recovery of irradiated ammonium acetate at 4.2 K, measured away from tunnel resonance, following an initial disturbance of the quasiequilibrium by setting the magnetic field for 110 sec to 0.1475 T (open circles), 0.1600 T (triangles), and 0.1400 T (closed circles).

cles and triangles in Fig. 2 are obtained for initial values of the field of 0.1400 and 0.1575 T.

The antisymmetric shape function of Fig. 1 is strongly reminiscent of the response of an NMR spectrum after off-resonance saturation, and of the dynamic polarization signal due to the solid effect.[1,13] In both these cases spectral diffusion plays a crucial role. The explanation of our results follows along similar lines.

The spin Hamiltonian for a single electron and its neighboring methyl groups is

$$\begin{aligned}\mathcal{H} &= \mathcal{H}_t + \mathcal{H}_{dt} + \mathcal{H}_s + \mathcal{H}_Z + \mathcal{H}_D\\ &= \hbar\omega_m \sum_i \sigma_z^{\,i} + \hbar \sum_i \Delta\omega_i \sigma_z^{\,i} + \hbar\omega_s S_z\\ &\qquad - \hbar\omega_p \sum_i \sum_{k=1}^{3} I_z^{\,ik} + \mathcal{H}_D.\end{aligned}$$

Here $\sigma_z^{\,i}$ is a fictitious spin-$\frac{1}{2}$ operator to give the tunnel splitting $\hbar(\omega_m + \Delta\omega_i)$ of methyl group i, ω_m being the mean tunnel frequency and $\Delta\omega_i$ distributed about this mean with a distribution function $g(\Delta\omega)$, normalized so that $\int g(\Delta\omega)\,d\omega = 1$; $\mathcal{H}_s$, $\mathcal{H}_Z$, and $\mathcal{H}_D$ are the electronic and nuclear Zeeman interactions and the dipole-dipole interactions.

Due to rapid electron-spin–lattice relaxation the expectation value $\langle S_z\rangle$ is always close to the thermal equilibrium value $-\frac{1}{4}\hbar\omega_s/k\theta_L$, where θ_L is the lattice temperature. The electron-proton dipole-dipole interaction causes $E \rightarrow A$ transitions of methyl groups satisfying $\omega_s = \omega_t + \Delta\omega_j$ (we neglect the relatively small quantity $\pm\,\omega_p$) at a rate proportional to $(\langle S_z\rangle - \langle \sigma_z^{\,j}\rangle) g(\omega_s - \omega_m)$. For experiments of relatively short duration so that $\langle \sigma_z^{\,j}\rangle$ does not change substantially, the dynamic nuclear polarization associated with these transitions is therefore proportional to $g(\omega_s - \omega_m)$. The transitions cause a change in $\langle \mathcal{H}_{dt}\rangle$ proportional to $\hbar(\omega_s - \omega_m)(\langle S_z\rangle - \langle \sigma_z^{\,j}\rangle) g(\omega_s - \omega_m)$. The proton-proton dipole-dipole interactions couple $\mathcal{H}_{dt}$ and $\mathcal{H}_Z$ so that a change in $\langle \mathcal{H}_{dt}\rangle$ induces a proportionate change in $\langle \mathcal{H}_Z\rangle$ as a consequence of SSD, also eliminating the hole in $\langle \sigma_z^{\,j}\rangle$ located at $\Delta\omega_j = \omega_s - \omega_m$.

The observed dynamic polarization is the sum of that generated as a result of the resonant contact with the electron and that due to subsequent SSD. The former is approximately proportional to $\pm g(\omega_s - \omega_m)$, the sign depending on the direction of the magnetic-field scan,[7] and the latter is proportional to $(\omega_s - \omega_m) g(\omega_s - \omega_m)$. The present results demonstrate the relative dominance of this contribution. There are two reasons for this dominance: (a) The contact with the electron generates dynamic polarization of both signs leading to a partial cancellation; and (b) since $\langle \Delta\omega^2\rangle^{1/2} > \omega_p$, there may be several SSD transitions for each initial transition involving the electron spin.

The observed resonance is a convolution of the distribution function $g(\omega_s - \omega_m)$ with the ESR spectrum of the free radicals. The latter have the structure $\mathrm{H_2\dot{C}\cdot COOH}$ and give rise at low temperature to an anisotropic four-line ESR spectrum.[12] The powder average of this spectrum may be approximated by a Gaussian shape of width [full width at half maximum (FWHM)] 0.005 T. If $g(\Delta\omega)$ also has a Gaussian form then the nuclear polarization due to tunnel diffusion is given by $(\omega_s - \omega_m)\exp[-\frac{1}{2}\alpha(\omega_s - \omega_m)^2]$, where $1/\alpha$ is the sum of the second moments of $g(\Delta\omega)$ and the ESR spectrum. When the two curves of Fig. 1(a) are added to eliminate hysteresis, a good fit to this function is obtained. From this we find that $g(\Delta\omega)$ has a width (FWHM) of 280 MHz, and $\omega_m/2\pi = 4.05 \pm 0.02$ GHz.

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