Experimental Evidence for Dynamic Nuclear Polarization by Cooling of Electron Spin-Spin Interactions

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(Received 1 March 1971)

Comparison of deuteron and proton dynamic polarizations measured simultaneously in butanol samples doped with porphyrexide, a free radical, shows that these polarizations correspond to equal spin temperatures for these different nuclei, in agreement with effects of dynamic orientation of nuclei by cooling of electron interactions, and in disagreement with the solid-state effect.

Since the beginning of dynamic polarization of nuclei by electron-nucleus dipolar coupling, a few mechanisms, the "solid-state effect",[1] the "cross effect",[2] and dynamic orientation of nuclei by cooling of electron interactions[3] have been proposed as the cause of the polarization. However, predictions of *absolute* polarization values by models not involving adjustable parameters have rather failed to agree quantitatively with experimental observations,[4] and models with a reasonable quantitative success have involved adjustable parameters, the physical meaning of which was difficult to ascertain.[2] This situation comes from the existence of experimental complications such as extra relaxation rates for the nuclei ("leakage"), the phonon bottleneck, or lattice heating due to its finite heat conductivity, especially at low temperatures, all of which cause a decrease in the nuclear polarization and are difficult to introduce into the theory without some degree of arbitrariness.

There is a clean test of these effects which consists in measuring the polarization obtained for two (or more) different nuclear species contained in a given sample and plotting one against the other. In this manner, unknown or poorly known quantities often disappear or have their influence considerably reduced. We have done this test for protons and deuterons. Measurements of their respective polarizations P_H and P_D were performed in 98% perdeuterated 1-butanol, C_4D_9OD, doped with porphyrexide, a free radical.[5] The protons were those of the 2% unsubstituted hydrogen atoms. Figure 1 shows the experimental results on a (P_D, P_H) plot. A few points were obtained at 25 kOe, either at a constant temperature of 0.51°K by varying the frequency of the polarizing rf field, or at the optimum rf frequency by varying the temperature between 0.51 and 1.0°K. One point comes from measurements at 50 kOe and 1°K.[6] Another point was measured in an ethanol sample, C_2D_5OD, at 25 kOe and 1°K. This experimental information will now be compared with

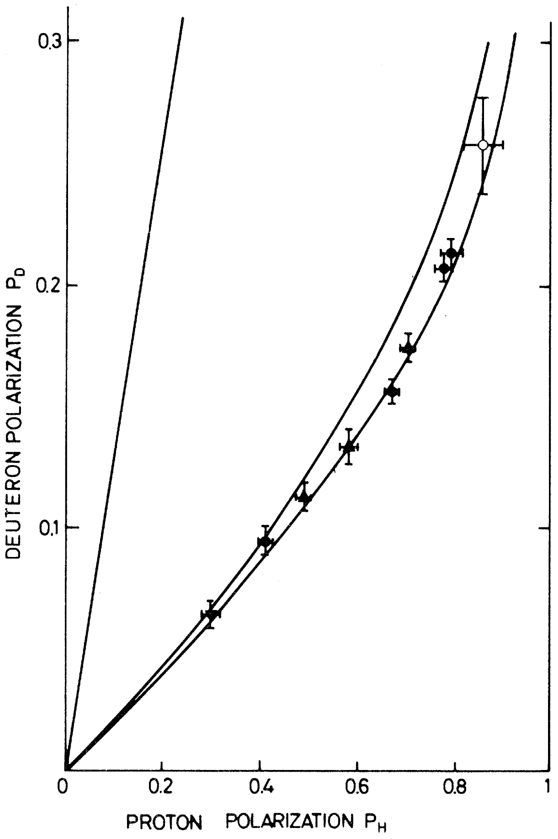

FIG. 1. The polarization P_H and P_D of protons and deuterons as measured in perdeuterated alcohols doped with porphyrexide, on a (P_D, P_H) plot: closed circle, 1-butanol, 25 kOe, 0.51°K at various microwave frequencies; upright triangle, 1-butanol, 25 kOe, optimum frequency, between 0.51 and 1°K; open circle, 1-butanol, 50 kOe, 1°K, optimum frequency; inverted triangle, ethanol, 25 kOe, 1°K, optimum frequency. Straight line, solid-state effect; upper curve, cross effect; lower curve, dynamic orientation of nuclei by cooling of electron interactions.

theoretical expectations.

Solid-state effect.[1]–There is little doubt that the solid-state effect is responsible for dynamic polarization of nuclear spins I in samples which contain electron spins S having a resonance line (ESR line) with a width much smaller than the nuclear Larmor frequency ω_I, i.e., when the frequencies $\omega_S+\omega_I$ and $\omega_S-\omega_I$ are well resolved from the ESR line centered at ω_S. As is well known, the solid-state effect tends to change the ratio of the populations of adjacent nuclear spin levels from its thermal equilibrium value $\exp(\hbar\omega_I/kT)$, where T is the lattice temperature, to the "enhanced" value $\exp(\pm\hbar\omega_S/kT)$ through the application of an rf field of frequency $\omega=\omega_S\pm\omega_I$. The nuclear polarization thus becomes, in an ideal case,

$$P_I=\pm\mathcal{B}_I(\hbar\omega_S/kT)\qquad\text{(ideal solid-state effect)}.\qquad(1)$$

$\mathcal{B}_I$ is the corresponding Brillouin function. In particular, proton and deuteron polarizations can be written as a function of the thermal-equilibrium electron-spin polarization, $P_e=\tanh(\hbar\omega_S/2kT)$, as

$$P_\mathrm{H}=P_{1/2}=P_e,\quad P_\mathrm{D}=P_1=4P_e/(3+P_e^2).\qquad(2)$$

The ideal solid-state effect thus predicts a unique curve on the $(P_\mathrm{D},P_\mathrm{H})$ plot; it is shown on Fig. 1.

When the ESR line is broad compared with the nuclear Larmor frequency, because of a distribution of individual electron-spin resonance frequencies, for example, as in amorphous samples doped with free radicals, the situation is more complex. Butanol doped with porphyrexide is a particularly important example of this case in view of its use in polarized-proton[7,8] and -deuteron targets.[5] The solid-state effect then takes the form of the "differential solid-state effect"[8,9]: The nuclei located around the electron spins S^+ having a resonance frequency $\omega_S^{\;+}$ such that $\omega=\omega_S^{\;+}+\omega_I$ –where ω is still the rf field frequency–tend to acquire a polarization equal to $-\mathcal{B}_I(\hbar\omega_S^{\;+}/kT)$, and the nuclei around the spins S^-, with resonance frequencies $\omega_S^{\;-}$ such that $\omega=\omega_S-\omega_I$, tend to acquire the *opposite* polarization through the solid-state effect. These two kinds of electrons thus oppose their contributions to the nuclear polarization. The average polarization of the sample is obtained by averaging over these two contributions, taking into account nuclear-spin diffusion. A precise treatment of the differential solid-state effect involves many unknowns such as dipolar coupling parameters and electron-spin–packet line shapes, and accurate predictions of the polarizations are difficult. We have not shown any corresponding curve on Fig. 1, because, by varying the parameters of various descriptions of the model,[10,11] we have obtained families of curves, none of which resembles the experimental trend.

Cross effect.[2]–This effect can only exist with systems of electron spins having a distribution of resonance frequencies. Nuclear polarization comes from cross-relaxation transitions between electron spins having resonance frequencies $\omega_S{}'$ and $\omega_S{}''$ such that $\omega_S{}'\pm\omega_S{}''=\pm\omega_I$, *and* from the applied rf field with frequency ω supposedly saturating the polarization of the electrons having resonance frequencies around ω, thus "burning a hole" in the ESR line. This model has been applied with a reasonable degree of success to describe early results on dynamic polarization of protons in 1-butanol (C_4H_9OH) samples doped with porphyrexide.[8] It involves a few arbitrary parameters; one is the ratio of the contributions to the nuclear spin-lattice relaxation rate of processes induced by the electron spin-lattice relaxation and by the electron spin-spin relaxation, respectively. The shape of the "hole" is taken to be a Gaussian with an arbitrary width Ω. We have extended this model to our deuterated samples, with the following changes: Nuclear-spin diffusion has been introduced, as without it, it seems unlikely that one would get any sizable magnetization in macroscopic samples; this changes Hwang and Hill's expression[12] for the final nuclear polarization by replacing the average of the ratio of two expressions by the ratio of their averages. Assuming fast spin diffusion, for example, one gets, for nuclear spins $\frac{1}{2}$,

$$P_{1/2}=\frac{\int g[g^-(P-P^-)-g^+(P-P^+)]dx}{\int g[\beta_0(1-P_0P)+g^-(1-PP^-)+g^+(1-PP^+)]dx},\qquad(3)$$

where $g\equiv g(x)$ is the ESR line shape with $g^+=g(x+\omega_I)$ and $g^-=g(x-\omega_I)$;

$$P\equiv P(x)=P_0\left[1-\frac{\tan\omega}{\langle\lambda\rangle+\tan\omega}\lambda(x-\omega)\right]$$

represents the electron-spin packet polarization under the action of the rf field, the intensity of which is described by t; $P^+=P(x+\omega_I)$, $P^-=P(x-\omega_I)$. λ is a Gaussian satisfying the conditions $\lambda(0)=1$, $\int\lambda(x)dx=\Omega$. We have taken Ω equal to 75 Oe instead of 100 Oe[8] in order to fit our measured value of the proton polarization equal to 79% at 0.51°K. The extension of Eq. (3) to the spin-1 deuterons has been done by multiplying the terms $P(x)-P(x\pm\omega_I)$ by $\frac{1}{3}(4-A)$, where $A=\langle 3I_z^2-2\rangle$. A is related to P_1 by $A^2-4A+3P_1^2=0$ when the deuteron spin system may be described by a spin temperature. The resulting curve is shown on Fig. 1. Such a (P_D, P_H) plot is much less sensitive to the variation of the parameters than are the absolute values: The curves corresponding to values of Ω varying between 75 and 100 Oe, for example, coincide within 1% with the curve shown, whereas the computed proton polarization at 0.5°K is 79% for $\Omega=75$ Oe and 63% for $\Omega=100$ Oe.

Dynamic orientation of nuclei by cooling of electron interactions. —Here, the various electron spins are supposed to make a collective response to the action of the applied rf field which is characterized by a common spin temperature T_s, defined in a suitable reference frame.[4,13] T_s can be smaller than the lattice temperature T by a few orders of magnitude. Several types of spin transitions then tend to give a spin temperature equal to T_s to the nuclei present in the sample. The nuclear polarization corresponding to these effects is given by

$$P_I=\mathcal{B}_I(\hbar\omega_I/kT_s), \tag{4}$$

i.e.,

$$P_\text{H}=\tanh(\hbar\omega_\text{H}/2kT_s),$$

$$P_\text{D}=4\tanh(\hbar\omega_\text{D}/2kT_s)\times[3+\tanh^2(\hbar\omega_\text{D}/2kT_s)]^{-1}. \tag{5}$$

The dynamic orientation of nuclei by cooling of electron interactions thus predicts that the nuclei of different nuclear species contained in a given sample all acquire the *same* spin temperature. This is to be contrasted with the solid-state effect which predicts through Eq. (1) that they acquire *different* temperatures $T_I=\pm\omega_I/\omega_S$, depending on their respective Larmor frequencies: Proton and deuteron spin temperatures as predicted by the solid-state effect thus differ by a factor of the order of 6. The common spin temperature T_s corresponding to dynamic orientation of nuclei by cooling of electron interactions may be computed very generally from the properties of the electron-spin system,[4] but the experimental complications mentioned above have prevented accurate absolute polarization calculations from being made until now. However, the theory predicts a unique curve on the (P_D, P_H) plot through Eq. (5); it is shown in Fig. 1.[14]

We insist on the fact that this curve depends on no other parameter than the ratio of the deuteron to the proton magnetic moment. It constitutes a unique prediction for samples in which this process is expected to be prominent.[15]

From the agreement between this last curve and the experimental points, we would tend to conclude that the state of the two nuclear species under dynamic polarization, in the samples considered, is describable by a single spin temperature, in agreement with the predictions of the dynamic orientation of nuclei by cooling of electron interactions and in disagreement with those of the solid-state effect.

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[12] With spin-diffusion-limited dynamic polarization, both integrands in Eq. (3) should be multiplied by $[\beta_0(1-P_0P)+g^-(1-PP^-)+g^+(1-PP^+)]^{-3/4}$. The corresponding curve on the (P_D, P_H) plot almost coincides with the "cross-effect" curve shown here.

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[14] If, instead of using the expression for $P(x)$ assumed by Hwang and Hill for the cross effect, we use the expression $P(x)=\tanh[\hbar(x-x')/2kT_s]$ with $x\equiv\omega_S$ and $x'\equiv\omega$, which corresponds to the hypothesis of a single spin temperature T_s for the *electrons* in a suitable ro-

tating frame of reference, the cross-effect terms in the rate equation for the polarization $p(x)$ of spin-$\frac{1}{2}$ nuclei, of the form $p(x)[1-P(x)P(x\pm\omega_I)]\pm[P(x)-P(x\pm\omega_I)]$, both became proportional to $p(x)-\tanh(\hbar\omega_I/2kT_S)$. This means that spin-$\frac{1}{2}$ nuclei tend to acquire a polarization just equal to that predicted by dynamic orientation of nuclei by cooling of electron interactions. This conclusion may be shown to be true for spin-1 nuclei as well; the cross effect thus reduces to an electron-interaction cooling effect. This explains why the corresponding curve on Fig. 1 is not very different from the unique spin-temperature prediction.

[15] Applying this model to other nuclei, one would predict, for example, a polarization of 26% for ^{13}C nuclei in perdeuterated 1-butanol doped with porphyrexide, at 0.5°K and 25 kG.

Accurate Calculation of the Low-Energy Electron-Diffraction Spectra of Al by the Layer–Korringa-Kohn-Rostoker Method

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(Received 26 April 1971)

Low-energy electron-diffraction spectra for three beams of Al {001} have been calculated from a complex static potential by a method of an accuracy comparable to modern band calculations. Despite the presence of strong attenuation, the spectra still show considerable structure which arises from the potential and which corresponds closely to experiment.

Several recent calculations[1-4] of low-energy electron-diffraction (LEED) spectra (i.e., the intensity of coherent elastically reflected electron flux from a crystal surface versus incident energy) for Al have given results which show encouraging agreement with the measured spectra. We find that a more precise calculation with a given potential provides a closer correspondence with experiment. Thus a more quantitative theory of LEED seems possible which links the scattering potential of the crystal to details of the spectrum. The present work will show the surprising extent to which this linking can be accomplished in Al with a static, complex, truncated bulk periodic scattering potential in the energy range 25 to 150 eV, despite the neglect of various surface and many-body effects.

In the work of Hoffstein and Boudreaux[1] (HB) who used the Fourier expansion (Bethe) method and a pseudopotential, the calculated spectra consist of groups of narrow lines which correspond suggestively to the broad measured lines out to 140 eV. However, detailed comparison of the HB theory with experiment is prevented by the restriction of the calculation to zero absorption and normal incidence of the electrons. In the work of Duke and Tucker,[2] by the inelastic-multiple-scattering method, it is shown that the main features of the spectrum can be obtained by simple selection of an s-wave–scattering phase shift and electron absorption.[3] However, the correspondence of theory and experiment is rough: The calculated secondary peaks are too small, and the calculated lines show little structure.[4]

In the present work, the spectra of a given complex static potential are calculated by a method of high accuracy (comparable to the accuracy achieved in band calculations). By means of a potential for Al whose real part is a self-consistent potential due to Snow[5] and whose imaginary part is taken from uniform-electron-gas theory,[6] this method is able to calculate the detailed structure of LEED peaks which show noteworthy correspondence with experiment. Not only do the spacings and widths of the peaks on three beams correspond closely, but structural details such as splittings, shoulders, and shapes appear to be significant. We note further the useful conclusion from comparison of the absorption-free (zero imaginary part) and full-absorption curves that the substantial experimental linewidths arise from the merging of whole clumps of elastic lines when absorption is introduced, and that the widths are rather greater than the broadening given by a simple (two-beam) theory of the effect of absorption.[7] The present