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Deuteron polarization of solid DT

P. C. Souers
Chemistry and Materials Science, Lawrence Livermore National Laboratory, Livermore, California 94550

P. A. Fedders
Department of Physics, Washington University, St. Louis, Missouri 63130

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Various possible means of attaining a large nuclear polarization of deuterons in solid deuterium tritide (DT) for use as a hydrogen-fusion fuel are considered. It is noted that dynamically polarized nuclear targets have reached only 40% polarization for deuterons despite there being no theoretical limit. In contrast, protons have been polarized to almost 100%. We consider dynamic nuclear polarization using both electrons as the pumping source (EDNP) and nuclei (NDNP). Most polarized targets have worked by EDNP thermal mixing. If protons are present, they bleed off part of the polarization intended for the deuterons. In a pure deuterated material, the smaller deuteron magnetic moment has so far prevented adequate nuclear cooling. The method most likely to work is the EDNP solid-state effect, which requires a narrow ESR spectrum for the atoms in solid DT. Should the tritons be polarized, their polarization can be transferred to the deuterons. Using NDNP thermal mixing, again, only 40% deuteron polarization is obtained. Using the NDNP solid-state effect and many polarization cycles, over 90% is achieved. The calculations offer optimism regarding deuteron polarization as far as the state of present knowledge of the properties of solid DT is concerned.

I. INTRODUCTION

The prospect of nuclear spin polarization of deuterium-tritium (DT) is an exciting new idea discovered by Kulsrud, Furth, Valeo, and Goldhaber.[1] If the triton and deuteron magnetic moments are aligned completely parallel, the heavy-hydrogen fusion cross section should increase by 50%. More showed that this polarization should last during the laser shot that ignites the DT.[2] Pan and Hatchett showed that the cost of a fusion system might be cut in half with spin-polarized fuel.[3]

We have undertaken to try to polarize solid DT. Most of our work has centered about the short longitudinal nuclear relaxation time of the triton T_{1_n} which must be substantially lengthened for successful polarization.[4,5] It became clear in this work that the optimum form of the heavy hydrogen is pure molecular DT (as opposed to the normal radiation-equilibrated mixture of D_2-DT-T_2).[5] Because of the tritium radioactivity, we felt that solid DT cannot be cooled to the mK temperatures needed for brute-force polarization. Instead, dynamic nuclear polarization (DNP) will have to be used. We have also measured the thermal conductivity of solid deuterium-tritium and shown that the triton memory time must be lengthened in order to remove the heat of DNP.[6] We now turn our attention to the deuteron, which has a magnetic moment μ_D of 4.331×10^{-27} J/T in DT. Because this is smaller than the triton magnetic moment μ_T of 15.05×10^{-27} J/T in DT,[7] we expected a longer and less troublesome nuclear relaxation time for the deuteron. We turn now to consider the properties of the deuteron.

The deuteron has a spin of 1 and in a dc magnetic field, there are three sublevels with magnetic quantum numbers $m_D=1, 0, -1$ and populations n_+, n_0, and n_-. In fact, the energy differences between the three levels are slightly different because of the interaction with the deuteron's quadrupole moment. Two peaks then appear in the nuclear magnetic resonance (NMR) spectrum. The lower frequency (energy) NMR peak of area A is proportional to n_+-n_0. The higher frequency (energy) NMR peak of area B is proportional to n_0-n_-. The ratio $R=A/B$ is usually calculated. A spin temperature is assumed to exist, and the sublevels are assumed to be equally spaced. Then,

$$R=\frac{n_+}{n_0}=\frac{n_0}{n_-} . \tag{1}$$

The vector polarization of the deuteron, P_D is[8]

$$P_D=\frac{n_+-n_-}{n}=\frac{R^2-1}{R^2+R+1} . \tag{2}$$

This polarization appears in the deuteron magnetization M_D according to

$$M_D=N\mu_D P_D , \tag{3}$$

where N is the density of nuclei. The magnetic energy is proportional to P_D, and this is what is measured for polarized targets. However, it is not what we want for spin polarization. In this case, we want all deuterons in one sublevel, e.g., n_+. To describe this, we define a fusion polarization Z_D given by[9]

$$Z_D(n_+)=\tfrac{3}{4}P_D+\tfrac{1}{4}Q_D=\frac{2n_+-n_0-n_-}{2n} . \tag{4}$$

The n_+ in parenthesis means that it is the $m_D=+1$ sublevel that we are trying to concentrate the nuclear population into. The term Q_D is the tensor polarization of the deuteron. It is a measure of the filling of the $m_D=0$ nuclear sublevel. It exists for the spin-1 deuteron but not the spin-$\frac{1}{2}$ proton or triton. When $n_+\rightarrow 1$, $Z_D\rightarrow 1$, we have

$$Z_D(n_+)=\frac{2R^2-R-1}{2(R^2+R+1)}\ , \tag{5}$$

where $R>1$.

With a defined nuclear spin temperature T we may write, from Eqs. (2) and (4)

$$Z_D(n_+)=\frac{2\exp(x_D)-1-\exp(-x_D)}{2[\exp(x_D)+1+\exp(-x_D)]}\ , \tag{6}$$

where

$$x_D=\frac{\mu_D B}{kT}\ . \tag{7}$$

Here B is the intensity of the applied dc magnetic field and k is Boltzmann's constant.

Generally, DNP is carried out by transferring the brute-force polarization of unpaired electrons in the sample to the surrounding nuclei. This is done by irradiating with microwaves just off the electron-spin resonance (ESR) frequency. Almost all polarized targets used in high-energy physics are made by this method. For such electron-nuclear polarization transfer (EDNP), P_D can usually not be greater than P_0, the electron polarization created by the dc magnetic field before the microwave pump needed for EDNP is turned on. Because the electron has a spin $\frac{1}{2}$,

$$P_0=\tanh x_e\ , \tag{8}$$

where

$$x_e=\frac{|\mu_e|B}{kT}\ . \tag{9}$$

Here μ_e is the magnetic moment of the electron (absolute value 9.285×10^{-24} J/T). Using Eq. (9), we calculate the parameters needed for 95% electron polarization. At 4.2 K, we require an 11.5 T magnetic field; at 1.4 K, 3.8 T; and at 0.5 K, only 1.4 T.

The well-known review article of Abragam and Goldman reduced EDNP to two basic mechanisms.[10] The solid-state (or solid) effect works by pumping a double ESR-NMR transition, which is followed by ESR relaxation. In its pure form, it works only if the ESR linewidth is so small that is does not overlap the double transitions at the frequencies $\nu_e\pm\nu_n$, where ν_e is the ESR frequency and ν_n the NMR frequency. If it does, the strongly allowed ESR transition swamps out the double transition.[11] There is a variation called the differential solid-state effect, which is supposed to work with broad ESR lines,[12] and is invoked for solid ammonia, the most successful of the current deuteron polarized targets.[13]

The second mechanism of EDNP is thermal mixing (or dynamic cooling). Here, the off-resonance microwave radiation cools the non-Zeeman electron spectrum. It does this by creating a population gradient in the electrons so that the colder ones will take energy from the nuclear magnetic moments.[14,15] Because of the thermodynamic aspect of the mechanism, spin temperatures are employed in its description.[16,17] By contrast, it is not clear that spin temperatures can even be defined in the solid-state effect.

II. DEUTERON POLARIZATION IN THE LITERATURE

For the decade of the 1970's, the polarized target materials of choice were the ethane and propanediols doped with paramagnetic porphyrexide or the chromium-V ion. There are two variations. In the earlier work, the compounds were only partly deuterated with an almost equal number of protons being present.[18–20] In the later work, the deuterium was enriched to 99% with only 1% being protium.[21,22] In both cases, the highest achieved vector polarization of the deuterons was only 40%. It is not clear then what limits the achieved deuteron polarization in these nearly pure compounds. We note that the proton and triton have the same nuclear spin of $\frac{1}{2}$. Also, the proton magnetic moment is 14.11×10^{-27} J/T,[7] almost as large as that of the triton. Whatever we can learn about the nuclear behavior of protonated compounds may carry over to solid DT.

In the 1980's the most popular polarized target material has been solid ammonia. Here, the highest deuteron polarization has been achieved by Meyer *et al.*[13] They obtained a vector polarization of 49% and a tensor polarization of 19%. If we assume an equal spin temperature (EST) between all deuterons, this translates to a fusion polarization Z_n of 41.5%. This record number, of course, has to be greatly improved in order to be of help to inertial confinement fusion.

The diols were considered the classic case of EDNP thermal mixing. A corollary of the mechanism was that protons and deuterons would be brought to EST by the non-Zeeman spectrum. It was the absence of EST between these nuclei that has led to the uncertainty of the mechanism in solid ammonia.[23] The ESR line is broad enough to overlap both the proton and deuteron sidebands at the 0.34 T field used in the work. However, the multiline ESR spectrum of ND_2 radicals makes the analysis difficult. There is, in fact, a "hole" in the ESR spectrum just where the proton sideband would be expected. It was these difficulties that led to the suggestion of the differential solid-state effect.

In contrast to the 40% deuteron polarization noted above, the protons in these same compounds can be polarized to 93–98%.[18,24] There is, however, no evident theoretical barrier to a high deuteron polarization. If all electron polarization could be transferred to deuterons at 3.35 T and 0.5 K (where a convenient 94-GHz microwave source is to be had), then Z_n will be 98.5%.

Finally, we mention lithium deuteride, which has reported 70% polarization.[25] However, this is mostly represented by the Li^6 nucleus, itself with spin 1. The deuteron, however, is reported to be polarized to only 25%.

III. LONGITUDINAL DEUTERON RELAXATION TIME

We turn to the deuteron to see what its longitudinal nuclear relaxation time, T_{1n}, will be. We hope that this will be longer than the corresponding triton time. No data exists for DT, and we must turn to the nonradioactive analog HD.

We first consider the proton relaxation time T_1^* for solid HD containing $J=1$ H_2 impurity. This is described by the Moriya-Motizuki theory,[26] which states that the molecular electric quadruple moment of the $J=1$ molecules splits the $J=1$ rotational energy into a band of states. These states are close enough together that certain combinations are always at the nuclear Larmor frequency. Then, energy can flow from the nuclear magnetic system to the molecular rotation and thence to the crystal lattice. The free molecular rotation of the $J=1$ molecules is a nuclear magnetic short circuit. The theory predicts that:[5,26,27]

$$T_{1n}^*(\text{H in HD}) = \frac{I(I+1)[\text{HD}]+I^*(I^*+1)[J=1\ \text{H}_2]}{I^*(I^*+1)[J=1\ \text{H}_2]} T_{11}^* \quad (10)$$

The quantities in brackets are mol fractions. Also, I is the nuclear spin of the proton in HD and I^* the same for proton in $J=1$ H_2. The quantity T_{11} is an "inherent" nuclear relaxation time that usually is calculated from the data. Equation (10) describes the nuclear magnetic heat capacities of the two systems. The form of Eq. (10) indicates that all nuclear magnetic heat must flow to the rotational degree of freedom through the magnetic moments of the $J=1$ H_2. If the fraction of $J=1$ H_2 is x, then $[\text{HD}]=1-4/3x$ for the case of $n\text{H}_2$ as the impurity. We then have

$$T_{1n}^*(\text{H in HD}) = \frac{3+4x}{8x} T_{11}^* \ . \quad (11)$$

For the deuteron in HD, we use the theory in the same way, where the limiting energy pathway is now the $J=1$ D_2 impurity. We write

$$T_{1n}(\text{D in HD}) = \frac{2[\text{HD}]+5[J=0\ \text{D}_2]+2[J=1\ \text{D}_2]}{2[J=1\ \text{D}_2]} T_{11} \ . \quad (12)$$

In HD and $J=1$ D_2, the nuclear spin is 1. In $J=0$ D_2, it is 0 in $\frac{1}{6}$ of the states and 2 in the remaining $\frac{5}{6}$. This leads to the average of 5 for $I(I+1)$. If $n\text{D}_2$ is used, then $[J=0\ \text{D}_2]=2x$, $[J=1\ \text{D}_2]=x$, and $[\text{HD}]=1-3x$. We obtain the equation

$$T_{1n}(\text{D in HD}) = \frac{1+3x}{x} T_{11} \ . \quad (13)$$

In Table I we list the measured values for the proton and deuteron in solid HD taken by Mano and Honig.[28] The proton data agrees with other measurements by Weinhaus and Meyer[29] and by Hardy and Gaines,[30] but no other source of deuteron data is available. The most important result from Table I is that the deuteron's longitudinal relaxation time is much longer than that of the proton, especially at low $J=1$ concentrations. Because the triton is so similar to the proton, we expect similar behavior in solid DT *as long as the tritium radioactivity does not interfere.*

For solid D_2-DT-T_2, then, we expect an equation

$$T_{1n}(\text{D in DT}) = \frac{2[\text{DT}]+5[J=0\ \text{D}_2]+2[J=1\ \text{D}_2]}{2[J=1\ \text{D}_2]} T_{11} \ . \quad (14)$$

We should not be far wrong if we use the T_{11} values for the deuteron in HD given in Table I.

In conclusion, if we can lengthen the triton's relaxation

TABLE I. Comparative longitudinal nuclear relaxation time data (in seconds), T_{1n}, for the deuteron in solid HD at 1.2–1.3 K, where the determining variable is $J=1$ D_2. The relaxation time for the proton in solid HD at 4 K, T_{1n}^*, where the $J=1$ H_2 is the critical variable, is also listed for comparison. T_{11} is the inherent relaxation time of the deuteron.

$J=1$ fraction, x	T_{1n} (s) H in HD Honig 60 MHz	T_{1n} (s) D in HD Honig, 2.6 and 6.3 MHz	T_{11} (s) D in HD Honig, 2.6 and 6.3 MHz
0.40	0.31		
0.20	0.25		
0.10	0.13	6.3	0.48
0.06	0.060	6.3	0.32
0.04	0.033	6.3	0.23
0.02	0.022	7.1	0.13
0.01	0.025	11	0.11
0.006	0.030	16	0.094
0.004	0.038	26	0.10
0.002	0.150	150	0.30
0.001	0.60	2000	2.0
6×10^{-4}	1.5	12 500	7.5
2×10^{-4}	13		

time to a long enough value in solid DT, we may hope that the deuteron's relaxation time will be much longer. Long relaxation times would be pursued by purifying the molecular DT to low levels of both $J=1$ T_2 and $J=1$ D_2.

IV. ELECTRON-NUCLEAR MECHANISMS APPLIED TO SOLID DT

We next consider how EDNP could be applied to solid molecular deuterium tritide (DT). In our laboratory,[31] the linewidth of the D and T atom has recently been measured in a 3.5 K D-T mixture (25% T_2-50% DT-25% D_2) at 9 GHz. The peak-to-peak linewidth of the derivative of either atom's absorption signal is about 5.6 MHz. Not enough work has been done to tell whether this linewidth will change with the conditions of the solid DT. However, we may immediately consider two scenarios upon moving to the more likely polarization conditions of 94 GHz and 3.35 T.

A. Inhomogeneous ESR line

At 9 GHz, the solid-state effect is not possible, because the triton sidebands occur at ±15 MHz and the deuteron sidebands at ±2 MHz. The deuteron sideband overlaps the densest part of the ESR line, and the triton sideband will overlap the wings of the ESR line. In both cases, we expect direct ESR stimulation to cancel out the polarization action of the solid-state effect. At 94 GHz, the sidebands are ±152 and ±22 MHz, respectively. However, an ESR line, rendered inhomogeneous by internal magnetic fields, will expand uniformly to a 58-MHz linewidth, and the solid effect will remain thwarted. We will have the broad ESR-line case for both nuclei at all magnetic fields, so that both nuclei can only be polarized by thermal mixing.

By analogy with the diols,[32] we expect the ESR spectrum to bring the tritons and deuterons in solid DT to the same final nuclear spin temperature. For the deuteron, Eq. (6) tells us the final polarization, where T in Eq. (7) is the final, cold spin temperature. For the triton, the nuclear polarization, P_T, is

$$P_T=\frac{\exp(x_T)-\exp(-x_T)}{\exp(x_T)+\exp(-x_T)}\ , \tag{15}$$

where

$$x_T=\frac{\mu_T B}{kT}\ . \tag{16}$$

The energy E, removed in cooling from a "hot" crystal lattice temperature T_h, to a cold spin temperature T_c is

$$E=B[M(T_c)-M(T_h)]\ . \tag{17}$$

The energy equals the magnetic intensity times the change in nuclear magnetization. For the deuteron, Eq. (2) may be rewritten as

$$P_D=\frac{\exp(x_D)-\exp(-x_D)}{\exp(x_D)+1+\exp(-x_D)}\ . \tag{18}$$

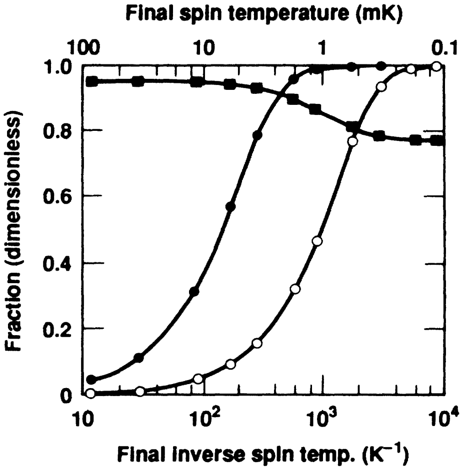

FIG. 1. Triton and deuteron polarization for EDNP thermal mixing from a "hot" 0.5-K lattice temperature to the same "cold" final spin temperature. The fraction of nuclear magnetic energy that is taken by the tritons during the cooling, i.e., most of it, is shown. The curves shown are triton polarization P_T (●), deuteron polarization Z_D (○), and the fraction of energy taken from the tritons (■).

In Fig. 1, we show the results for a sample with equal numbers of tritons and deuterons coupled so they will equilibrate to the same spin temperature. The sample starts at 0.5 K and various amounts of heat are taken out of the nuclear spin systems. Most of the heat is taken from the tritons, which thermally dominate the pair of nuclei. The tritons are more effectively polarized at a given spin temperature than the deuterons. The coldest anyone has apparently reached is about 1.65 mK, where the tritons are polarized near 100% but the deuterons only to 40%. There is, however, no theoretical limit to going colder.

We return to the polarized targets. If equal numbers of protons and deuterons are present, we expect a severe penalty to the deuterons for the partitioning of energy between the nuclei. If the spins cool from 0.5 K to mK temperatures, only 11% of the heat taken out comes from the deuterons. At first glance, an all-deuteron sample should cool further, but the deuteron's magnetic moment is only one-third that of the proton. This will weaken the interaction between the nuclei and the non-Zeeman electron spin system. We assume that this coupling is proportional to the weak dipolar coupling between the electron and nuclear spins. Then, the ratio of the deuteron-to-triton rate constant for polarization will go as the ratio of the nuclear magnetic moments: 0.288.[33] This reduces the all-deuteron sample cooling power to only 1.3 times that of the proton-deuteron sample. This leads to a 1.2-mK final spin temperature for a 52% vector polarization, which is not far off the best experimental value of 42% in diols[22] and 49% in ammonia.[13] As long as EDNP thermal mixing is the mechanism, all existing materials do not seem to be able to get the deuterons cold enough.

B. Homogenous ESR line

The 5.6-MHz ESR line is so narrow that it well may be homogeneous, i.e., one line with an instantaneous response anywhere on it. Then, it will remain at the same 5.6-MHz linewidth even at higher magnetic fields. At 3.35 T, the ±152-MHz triton sideband should lie far off the ESR line. The ±22-MHz deuteron sideband could still overlap the wings and nullify the solid-state effect. EDNP thermal mixing may still be needed to polarize the deuterons.

At higher field, the two types of nuclei are now decoupled, whereas at low field, they were linked together through their interaction with the electron spectrum. The possibility now exists of polarizing the deuterons without interference from the tritons.

The best situation to have is the solid-state effect for deuterons with there being no overlap with the ESR spectrum. To accomplish this, we might have to raise the magnetic field to 10 T and pump at hundreds of GHz. We have previously worked out the solid effect equations for the deuteron,[9] and we shall illustrate our point with the simple result for the triton. For a triton at high magnetic field, the steady-state nuclear polarization, $P_T(\mathrm{SS})$, will be[11]

$$P_T(\mathrm{SS})=\frac{\beta}{\beta+f(\beta+2)} . \tag{19}$$

Here β is the pumping parameter and f is a combination of longitudinal relaxation times and concentrations such that we require $f \ll 1$. For a triton we might hope to have $\beta=10$ and $f=0.01$, whereupon $P_T(\mathrm{SS})=0.99$. For the deuteron, β will be smaller by a factor of 0.144, because β is a function of the nuclear gyromagnetic rate.[11] However, the deuteron's longitudinal relaxation time could be 100 times longer than that of the triton, so that Eq. (19) predicts near-total deuteron polarization. Direct EDNP by the solid-state effect, should it be possible, seems to be the best way to go.

V. EFFECT OF SLOW SPIN DIFFUSION

We have assumed an infinitely fast spin diffusion; i.e., that the nuclear states will quickly transport themselves to the nearest hydrogen atom to be polarized. Let us consider N hydrogens per unit volume. Each atom is at the center of a sphere of radius $r=(3/4\pi N)^{1/3}$. The approximate diffusion coefficient in this sphere will be[34]

$$D \cong \frac{r^2}{4t_d} . \tag{20}$$

Here t_d is the diffusion time. For large polarization $t_d \ll T_{1n}$. Then, we have

$$D > \frac{1}{4T_{1n}}\left[\frac{3}{4\pi N}\right]^{2/3} . \tag{21}$$

In preliminary ESR work on the solid D-T mixture, we have found an atom density of about 200 ppm at 4 K.[31] We expect a solid density of 51 500 mol/m (Refs. 3 and 35) so that $N \sim 6\times10^{24}$ atoms/m.[3] We take $T_{1n} \sim 2000$ s, the value for $x=0.001$—a DT purity that should be obtainable. Using Eq. (21), we obtain

$$D > 1.5\times10^{-21}\ \mathrm{m^2/s} . \tag{22}$$

We know of no measured deuteron spin-diffusion coefficients, but we may compare these with values obtained for protons and fluorine-19. In yttrium ethyl sulfate a value of $4.3\times10^{-16}\ \mathrm{m^2/s}$ was directly measured at 1.1 K by Gates and Potter.[36] Nakamura and Fuijo calculate $3.1\times10^{-16}\ \mathrm{m^2/s}$ for protons in solid HD.[37] Two studies have been made of $\mathrm{CaF_2}$ doped with ions containing free electrons.[38,39] A study of the relaxation time T_{1n} of the F^{19} nuclei at 80–180 K has produced spin diffusion values of 8×10^{-17} to $4\times10^{-16}\ \mathrm{m^2/s}$. These values are much larger than that of Eq. (22), but there is reason to expect slower diffusion for the deuteron. We have earlier mentioned that varying electric fields in the crystal interact with the nuclear quadrupole moment and split the NMR line into two parts. If these two parts do not overlap in frequency, it was believed that the deuterons cannot communicate by spin diffusion.[40] However, some spin diffusion has been found even in this case,[41] so that the detailed mechanism remains to be described. It is possible that slow spin diffusion could be affecting the polarization in the all-deuterated polarized target materials.

Fedders has considered the case of solid HD and finds that deuteron spin diffusion is speeded up by the presence of the protons. He notes that in most nuclear-spin systems the nuclear magnetization is readily transported via mutual spin flips induced by the dipolar interaction. By a mutual spin flip we mean the spin conserving process whereby one spin flips up (down) and a neighboring spin flips down (up). A band[42] with a width of order ν_d, where ν_d is the frequency characterizing the magnitude of the dipolar interaction, is formed about the Larmor frequency ν_n of an individual spin. The transport of nuclear spin magnetization and the formation of the band of states is relatively unaffected by inhomogeneous line broadening that is small compared to ν_d. In this case, in the absence of any other mechanism, there will be no spin diffusion.

Recently several authors[43-46] have investigated spin diffusion in the limit of large inhomogeneous broadening where the mechanism depends on the existence of transverse spin fluctuation from an independent source such as phonons or another reservoir of spins. In the present context this means that the spin fluctuations induced by the H nuclear spins in HD can cause spin diffusion among the D nuclear spins even though the D nuclear spins undergo considerable inhomogeneous broadening from defect-induced electric field gradients. Fedders calculates the diffusion coefficient for D in HD is calculated to be

$$D \simeq \frac{1.7\times10^{-17}}{\Delta\nu^2} , \tag{23}$$

where $\Delta\nu$ is the NMR linewidth in kHz.[46] For D in solid HD, Honig estimates this to be about 2 kHz at a 5-MHz NMR frequency.[47] This leads to a diffusion coefficient of

$$D \simeq 4\times10^{-18}\ m^2/\mathrm{s} . \tag{24}$$

Because we expect DT to act much like HD, this large coefficient indicates that slow spin diffusion is not expected to harm the deuteron polarization in solid DT.

VI. NUCLEAR-NUCLEAR THERMAL MIXING

We shall consider next a different approach. We shall assume that the tritons in solid DT can be quickly and completely polarized (an event that has not yet happened). We shall consider how the triton polarization can be transferred to the deuteron by nuclear-to-nuclear polarization (NDNP). This technique was proposed and demonstrated by Honig and Mano on solid HD at low polarization.[48] Recently, it has been demonstrated with HD in a dilution refrigerator operating at 15 mK in a 13-T magnetic field, with substantial "brute-force" proton polarization and appreciable NDNP-transferred deuteron polarization.[49]

The case of solid DT will be different because of the 1 W/mol radioactive decay heat. In DT,[50] it seems unlikely that mK temperatures can ever be obtained with bulk samples. The sample temperature will be too high for brute-force polarization. Instead, the tritons will have to be polarized dynamically by EDNP. Then, the microwave source will be turned off, and the triton-to-deuteron polarization transfer by NDNP carried out. The tritons will be polarized again and the process repeated for as many cycles as possible. Of course, the entire process must take place in a time short compared to the deuteron relaxation time, T_{1n}, which we are assuming will be long.

We first consider NDNP mixing. The intent here is to polarize the tritons, then lower the dc magnetic field until the deuteron and triton NMR spectra overlap. Then, energy flows from the deuterons to the tritons until they both reach the same nuclear magnetic spin temperature. The greatest danger here is that T_{1n} will become too short at the low magnetic fields used for thermal mixing.

We have already calculated a related problem and discovered that the partitioning of energy between tritons and deuterons limited the ultimate deuteron polarization. It will be more difficult here, because the triton polarization cannot be replenished without a new EDNP sequence. As seen previously, the nuclear magnetic energy equals the dc magnetic intensity times the change in the nuclear magnetization. The triton starts cold at a spin temperature T_c, which describes its large initial polarization. The energy gained by the triton is

$$E(\mathrm{T})=-N\mu_{\mathrm{T}}B\left\{\frac{\exp(x_{\mathrm{T}})-\exp(-x_{\mathrm{T}})}{\exp(x_{\mathrm{T}})+\exp(-x_{\mathrm{T}})}\right|_{T_c}^{T_f} . \qquad (25)$$

The final, warmer nuclear spin temperature is T_f, where $T_f > T_c$.

The energy lost by the deuteron is

$$E(\mathrm{D})=N\mu_{\mathrm{D}}B\left\{\frac{\exp(x_{\mathrm{D}})-\exp(-x_{\mathrm{D}})}{\exp(x_{\mathrm{D}})+1+\exp(-x_{\mathrm{D}})}\right|_{T_h}^{T_f} . \qquad (26)$$

The deuteron density N is the same as that of the triton, and T_h is the initial hot temperature of the crystal lattice, where $T_f \ll T_h$.

Figure 2 shows the result of our calculations, where we assume that the deuteron memory time is infinitely long. The best results are obtained for a crystal lattice temperature, i.e., a sample temperature T_h of 0.3 K or below. Above 0.8 K, the efficiency drops off rapidly. However, even at best, this procedure reaches only 40% deuteron polarization. Earlier, the partitioning of energy between nuclei limited deuteron polarization when we pumped both nuclei through the electron spectrum. We obtain the same 40% deuteron polarization here, because we are doing the same process, but now in two steps. This process is more inefficient because the intermediate system—that of the tritons—is limited in its capacity to absorb heat.

VII. NUCLEAR-NUCLEAR SOLID-STATE EFFECT

The tritons and deuterons in neighboring DT molecules interact with one another by way of the weak dipolar interaction. The energy level scheme is shown in Fig. 3. The magnetic sublevel quantum numbers are m_{T} and m_{D}, respectively, for the triton and deuteron. We assume that the initial EDNP has loaded all the tritons equally into the lower three $m_{\mathrm{T}}=\frac{1}{2}$ sublevels, i.e., that the initial triton polarization is 1. We next saturate the two radio-frequency transitions as shown. Electron spin relaxation then preferentially fills the lowest $m_{\mathrm{T}}=\frac{1}{2}$, $m_{\mathrm{D}}=1$ sublevel, so that the deuteron polarization will be positive. This technique, used for Li^7 and F^{19} in LiF Agragam and Proctor, was the first demonstration of the solid-state effect.[51] Since then, the name "solid-state effect" has been used almost exclusively for electron-to-nuclear polarization (EDNP).

Fedders and Souers have worked out the solid-state effect theory for the yet unrealized case of electron-to-deuteron polarization.[9] We may use these equations by simply converting the electron equation for use by the tri-

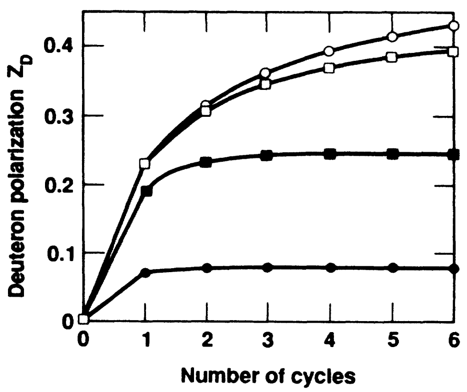

FIG. 2. Calculated deuteron polarization, Z_{D}, in solid DT after triton-to-deuteron NDNP thermal mixing. The temperatures below are those of the crystal lattice temperature T_h which is the initial deuteron temperature. The deuteron relaxation time T_{1n} is assumed to be infinitely long. The temperatures of the various curves are 0.1–0.3 K (○), 0.8 K (□), 1.4 K (■), and 4.2 K (●).

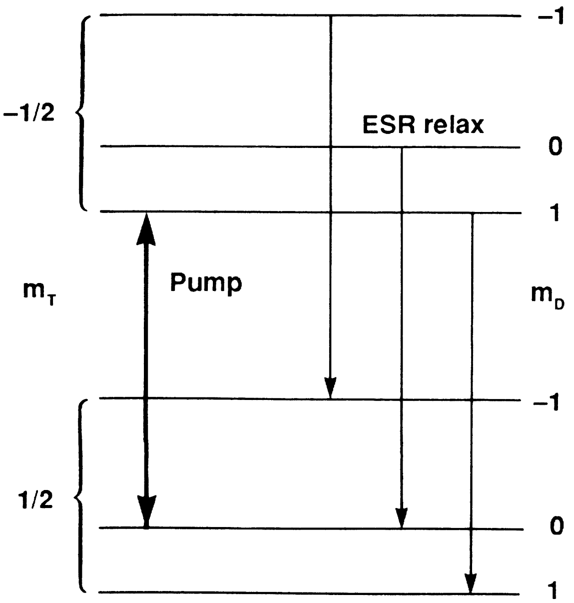

FIG. 3. Schematic of energy levels for the triton-deuteron system linked by weak dipolar coupling. The magnetic quantum numbers $m_{\rm T}$ and $m_{\rm D}$ are for the triton and deuteron, respectively. The pumping is shown and the ESR relaxation loads the lowest $m_{\rm T}=\frac{1}{2}$, $m_{\rm D}=1$ sublevel, creating deuteron polarization by the NDNP solid-state effect.

ton. The one difference is that the triton polarization has no continuous regeneration by the dc magnetic field. The time constants associated with $P_{\rm T}$, $P_{\rm D}$, and $Q_{\rm D}$ are T_{1n}^*, T_{1n}, and T_{1q}, respectively. The first is the longitudinal triton relaxation time and the second two are deuteron relaxation times, where T_{1n} is the one measured by NMR. The constant β was previously defined for Eq. (19). The equations of motion, where no cross relaxation is considered, become

$$T_{1n}^*\frac{dP_{\rm T}}{dt}=-\frac{\beta}{2}[P_{\rm T}(\tfrac{4}{3}-\tfrac{1}{3}Q_{\rm D})-P_{\rm D}]-P_{\rm T}\ , \tag{27}$$

$$T_{1n}\frac{dP_{\rm D}}{dt}=-\frac{\beta}{4f_1}[P_{\rm D}-P_{\rm T}(\tfrac{4}{3}-\tfrac{1}{3}Q_{\rm D})]-P_{\rm D}\ , \tag{28}$$

$$T_{1q}\frac{dQ_{\rm D}}{dt}=-\frac{3\beta}{4f_2}(Q_{\rm D}-P_{\rm T}P_{\rm D})-Q_{\rm D}\ . \tag{29}$$

The coefficient f_1 equals T_{1n}^*/T_{1n}. In the case of electron polarization, an electron-to-nucleus ratio was included, but this ratio becomes equal to 1 for the case of DT. Also for EDNP, it was necessary to have $f_1 \ll 1$, which is easy to obtain in our case. We may consider solid HD data as a model for solid DT. We have seen in Table I that we expect $T_{1n} > T_{1n}^*$, so that f_1 would decline from 0.021 at $x=0.1$ to 10^{-4} at $x=0.0006$.

We next assume the anharmonic Raman process for nuclear spin-phonon decay,[52] even though it is probably not physically present. We set

$$T_{1q}=\tfrac{5}{3}T_{1n}\ . \tag{30}$$

$$f_2=\tfrac{3}{5}f_1\ . \tag{31}$$

This allows us to simplify Eq. (2.9) for the purposes of illustrating the basic physical principles to

$$T_{1n}\frac{dQ_{\rm D}}{dt}=-\frac{3\beta}{4f_1}(Q_{\rm D}-P_{\rm T}P_{\rm D})-\tfrac{3}{5}Q_{\rm D}\ . \tag{32}$$

We next consider the $1/e$ time constants to steady state polarization. In EDNP, the electron time constant was much smaller than that of the nuclei. This is not so for NDNP. We obtain the $1/e$ times for the triton $\tau_{\rm T}$ and for the deuteron $\tau_{\rm D}$ from Eqs. (27) and (28) for $\beta \gg 1$. We have $\tau_{\rm T}\simeq 3T_{1n}^*/2\beta$ and $\tau_{\rm D}\simeq 4f_1T_{1{\rm D}}/\beta$, so the ratio $\tau_{\rm T}/\tau_{\rm D}=\frac{3}{8}$. This shows that $\tau_{\rm T}\simeq\tau_{\rm D}$ for NDNP, and Eqs. (27), (28), and (32) must be solved simultaneously.

We have solved these equations using the high power of $\beta=10$ and $f_1=10^{-4}$. The results are shown in Fig. 4. The triton $P_{\rm T}$ decreases as polarization is transferred to the deuteron $Z_{\rm D}$. We note also the slower decay of $P_{\rm T}$ with $\beta=0$. For pure ESR relaxation, the solid-state effect reverses and the deuteron polarization flows back to the tritons. Clearly, the highest deuteron polarization is obtained when $P_{\rm T}\simeq Z_{\rm D}$, i.e., at about $0.3T_{1n}^*$. At longer times, both polarizations decline with T_{1n}.

We next go to a pulse sequence. First, the tritons are polarized at microwave frequencies by EDNP. The time of the triton polarization is considered to be infinitely fast compared to the next step, which is the radio-frequency triton-to-deuteron polarization. Thus, two sources are used alternately, and they must be gated on and off. For a 94-GHz EDNP frequency, the difference of the triton and deuteron NMR frequencies is needed. The NDNP frequency would then be 130 MHz. The radio-frequency source is allowed to run until $Z_{\rm D}$ is at a maximum. This occurs when $Z_{\rm D}\geq P_{\rm T}$. Then, the tritons are quickly re-

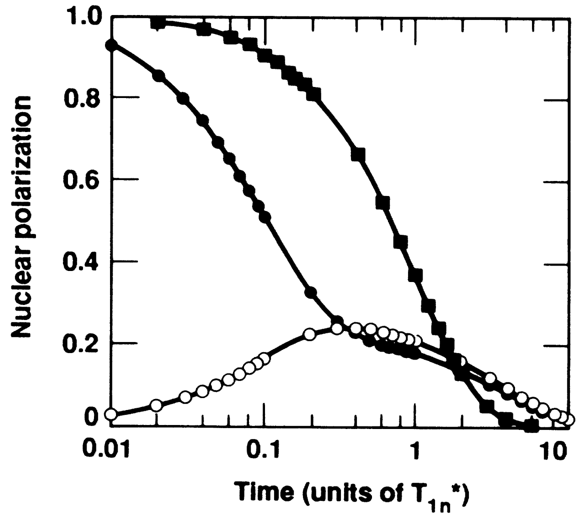

FIG. 4. Calculated NDNP solid-state transfer of polarization from tritons to deuterons in solid DT in a single cycle. The curve for the triton polarization $P_{\rm T}$ with $\beta=0$, is shown by (■). With the power parameter β equal to 10, the triton polarization is given by (●) and the deuteron polarization $Z_{\rm D}$ by (○).

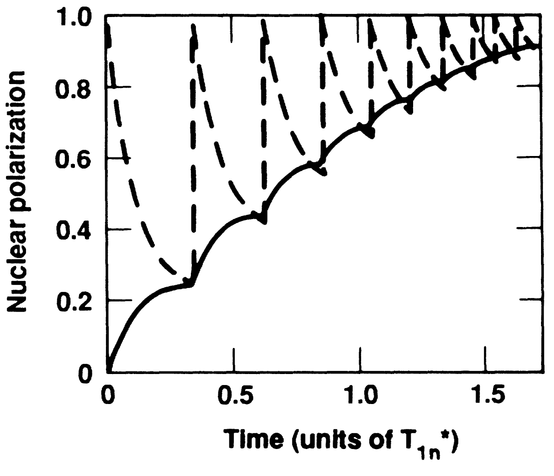

FIG. 5. Ten cycles of NDNP triton-to-deuteron polarization using the solid-state effect. The tritons (dashed line) are repolarized by EDNP at the start of every cycle. The deuteron polarization is shown by the unbroken line.

polarized and the cycle is repeated, except that this time the deuterons start with partial polarization. In our model, we assume that $T_{1n}/T^*_{1n}=10^4$, and we run for 10 cycles. The results are shown in Fig. 5, where we find a calculated deuteron polarization of over 90%. This is the best result obtained by any method so far. Another advantage of this approach is that the nuclear-nuclear interaction takes place between neighboring molecules, so that slow spin diffusion, if it did exist, would not affect the result. Further analysis shows that the efficiency of polarization is only decreased a few precent by allowing T_{1n}/T^*_{1n} to decrease to as low as 10. For $T_{1n}/T^*_{1n}=1$, however, the deuteron polarization is cut virtually in half.

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