Although the value of $p_{e\perp}$ required to fit the data is only half that estimated above, this discrepancy disappears if one assumes that the value of A in Eq. (1) is an order of magnitude smaller than the theoretical estimate of L-J; other data on proton relaxation[6] and dependence of enhancement on pulse width are in agreement with this assumption. The measured build-up rate versus $1/\tau$ was found to agree with Eq. (3b), using the above parameters. The build-up time is 6 min for $\tau = 0.05$ sec. Further experiments at $H_p = 20$ kOe have yielded a proton polarization of 35% for $\tau = 0.1$ sec.

To summarize, we have achieved appreciable proton polarizations in Yb:YEtSO$_4$, the magnitude and build-up rate being both reasonably explained by Eqs. (3). We have no evidence yet whether or not cross relaxation involving two or more proton spin flips per Yb^{3+} spin flip is important; this is the only process that could prevent the protons from acquiring the full Yb^{3+} polarization. The build-up time can probably be made as small as 1% of the proton-relaxation time by pulsing more frequently than our apparatus would allow. It is furthermore not unreasonable to expect that polarizations twice the value reported here could be obtained by using a more suitable pulse shape: wider to allow sufficient time to polarize the Yb^{3+} fully, and with a rapid cutoff to prevent depolar-

ization. The dc and pulsed fields need not be very homogeneous, permitting an open structure with good beam access in polarized target applications. In this sense this method may have advantages over the dynamic microwave method,[7,8] besides being basically simpler.

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[1]K. H. Langley and C. D. Jeffries, Phys. Rev. Letters 13, 808 (1964).

[2]C. D. Jeffries, Cryogen. 3, 41 (1963).

[3]A. Abragam, Cryogen. 3, 42 (1963).

[4]K. H. Langley, private communication. A proton polarization of 18.5% has been observed in a crystal of YEtSO$_4$ containing 2% Yb^{172} at $T = 1.3°$K, $H = 10$ kOe, and 60 rps.

[5]N. Bloembergen, S. Shapiro, P. S. Pershan, and J. O. Artman, Phys. Rev. 114, 445 (1959). Equations (2) are also readily obtained from Eqs. (10) and (11) of Ref. 8 by neglecting the terms in w_1, w_3, and w_4.

[6]K. H. Langley and C. D. Jeffries, to be published.

[7]C. D. Jeffries, Dynamic Nuclear Orientation (John Wiley & Sons, Inc., New York, 1963).

[8]T. J. Schmugge and C. D. Jeffries, Phys. Rev. 138, A1785 (1965).

DYNAMIC POLARIZATION OF NUCLEI BY ELECTRON-NUCLEUS DIPOLAR COUPLING ("EFFET SOLIDE")

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A remarkable amount of results have been obtained at Berkeley by Jeffries and his collaborators[1-4] on the electron-spin relaxation in rare earth salts, particularly in crystals of lanthanum magnesium double nitrate (LMN) doped with neodymium and, in this case, on the hydrogen nuclei relaxation and their dynamic polarization[5] by "effet solide."[6] These results have led us to reconsider the theoretical description of this effect and of the relaxation of nuclei coupled by dipolar interactions with electronic spins. Our conclusions differ from those of Schmugge and Jeffries sometimes by factors of the order of 1000 or more; as "ef-

fet solide" has become a widely used method for producing polarized proton targets, we thought it worthwhile to give a brief description now, before publishing a more complete paper later.[7] Here we shall mainly be concerned with the stationary values of the nuclear polarization, first when there is no "leakage," i.e., no cause of nuclear relaxation other than the interaction with the electronic spins under consideration. In this case, nuclear spin diffusion does not control the stationary states; we suppose that there is no phonon bottleneck, then we introduce it, and we apply the results to the case of LMN, 1% Nd. We also consider the cases

in which there is "leakage;" the nature of spin diffusion is then very important, even to determine the stationary states, and we suppose here that it is very fast.

We consider N_e electronic spins S^i, and N_n nuclear spins I^j $(S = I = \frac{1}{2})$, coupled by dipolar interactions $D(I, S)$; $\omega_e = \gamma_e H$ and $\omega_n = \gamma_n H$ are their resonance frequencies in an applied static field H directed along an axis Oz; $P_0 = \tanh(\hbar\omega_e/2kT_0)$ is the electronic polarization at the temperature T_0 of the lattice; the electronic relaxation is attributed to a direct process; the electronic linewidth $\Delta\omega_e$ will be small compared to ω_n; the electronic line shape is expressed as $g(\omega)$, with

$$\int_{-\infty}^{+\infty} g(\omega)d\omega = 1.$$

One knows that it is then possible[8] to describe the spin system under the action of a radio-frequency field H_1 normal to H, of frequency $\omega = \omega_e + \omega_n$ or $\omega_e - \omega_n$, by the populations of the eigenstates of its static Hamiltonian. The spins S^i, supposed to be alike, all have the same polarization P_e, and $P_n{}^j$ will be the polarization of spin I^j. The coefficient ϵ_{ij} of mixing of eigenstates due to $D(I^j, S^i)$ is given by[9] $|\epsilon_{ij}| = (\frac{3}{4})\gamma_e \hbar H^{-1} R_{ij}{}^{-3} \sin\Theta_{ij} \cos\Theta_{ij}$, where R_{ij} is the distance between S^i and I^j, and Θ_{ij} the angle between Oz and the direction S^i-I^j. The spin system executes allowed electronic transitions in which $\Delta S_z{}^i = \pm 1$ and $\Delta I_z{}^j = 0$ for all j values, and transitions which are forbidden in the absence of dipolar coupling in which $\Delta S_z{}^i = \pm 1$, $\Delta I_z{}^j = \pm 1$ or ∓ 1 for one of the j values, and zero for the others.

1. No "leakage"; no phonon bottleneck. – The evolution of P_e is described by

$$\frac{dP_e}{dt} = -w\frac{(1 - \sum_j \epsilon_{ij}{}^2)^2}{(1 + \sum_j \epsilon_{ij}{}^2)^2}\left(\frac{P_e}{P_0} - 1\right) - w\frac{4\sum_j \epsilon_{ij}{}^2}{(1 + \sum_j \epsilon_{ij}{}^2)^2}$$

$$\times \left(\frac{P_e}{P_0} - 1\right) - W\frac{\sum_j 4\epsilon_{ij}{}^2(P_e \pm P_n{}^j)}{(1 + \sum_j \epsilon_{ij}{}^2)^2}, \quad (1)$$

where w/P_0 is the inverse of the spin S relaxation time, and W is the allowed transition probability that would induce an rf field of amplitude H_1 and of frequency equal to ω_e: $W = \gamma_e{}^2 H_0{}^2 \times g(\omega_e)$. w is temperature independent: We have separated the contribution of the allowed and of the forbidden transitions to the relaxation. The

factor $(1 + \sum_j \epsilon_j{}^2)^2$ comes from the normalization of the wave functions; $f = \sum_j \epsilon_{ij}{}^2$ is related to the contribution of the spins I^j to the second moment of the resonance line of the spins S^i by[9] $f \cong (\frac{3}{5})\Delta\omega_{IS}{}^2/\omega_n{}^2$. As here this line is narrow with respect to ω_n, f is smaller than unity (generally very much smaller) but cannot be neglected because of its important role in the presence of phonon bottleneck. We notice finally that Eq. (1) depends on nuclear spin diffusion only through the $P_n{}^j$.

The evolution of $P_n{}^j$ under the action of the dipolar coupling $D(I^j, S^i)$ and of the electronic relaxation as well as of the rf field H_1 reads[10]

$$\frac{\partial P_n{}^j}{\partial t} = -w\frac{\sum_i 4\epsilon_{ij}{}^2}{(1 + \sum_j \epsilon_{ij}{}^2)^2}\left(\frac{1}{P_0} - P_e\right)$$

$$-W\frac{\sum_i 4\epsilon_{ij}{}^2}{(1 + \sum_j \epsilon_{ij}{}^2)^2}(P_n{}^j \pm P_e), \quad (2)$$

where we have neglected $P_n{}^0 \cong \hbar\omega_n/2kT_0$ as being always smaller than P_0, and where $(1/P_0 - P_e)$ is a term introduced and justified to explain the proton relaxation in LMN, 1% Nd.[5] Terms which describe the nuclear spin diffusion, and which couple the polarization of neighboring nuclei, may add to the contribution $(\partial/\partial t) \times P_n{}^j$, but in stationary conditions, one sees that $\partial P_n{}^j/\partial t = 0$ does not depend on the particular spin I^j, and P_n being the unique value of $P_n{}^j$, Eqs. (1) and (2) become

$$w\left(\frac{P_e}{P_0} - 1\right) + W\frac{4f}{(1+f)^2}(P_e \pm P_n) = 0, \quad (1')$$

$$w(P_0{}^{-1} - P_e)P_n + W(P_n \pm P_e) = 0. \quad (2')$$

The system (I) = (1') + (2') does not depend on spin diffusion. The maximum absolute value $P_n{}^{max}$ of P_n is found by letting W be much greater than w; $P_n{}^{max}$ is, of course, smaller than or equal to P_0, but it is never smaller than $[1 - (1 - P_0{}^2)^{1/2}]/P_0$ (see Fig. 1) for any value of the dipolar coupling parameter $f = \sum_j \epsilon_{ij}{}^2$, in contradistinction with earlier theories.[5,11,12] The physical reason for the behavior of $P_n{}^{max}$ when P_0 approaches unity is clear: The electronic relaxation approaches a finite value, whereas the nuclear relaxation is slowed down by a factor of the order of $(1 - P_0{}^2) \cong 2(1 - P_0)$,
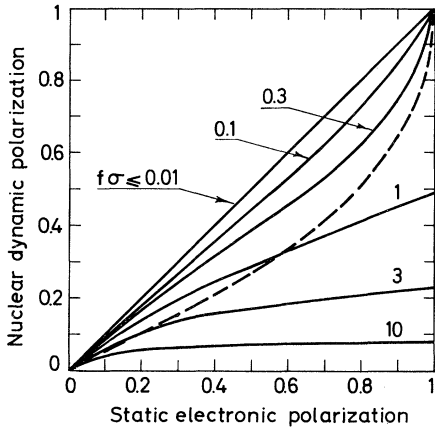
FIG. 1. No "leakage"; phonon bottleneck. Maximum dynamic polarization P_n^{max} vs thermal equilibrium electronic polarization P_0, for different values of $f\sigma'$ (f: dipolar coupling parameter; σ': phonon bottleneck parameter), with $f \ll 1$. The dotted line represents $[1-(1-P_0^2)^{1/2}]/P_0$ which is the lower limit of P_n^{max} when there is no "leakage" and no phonon bottleneck.

the dynamic polarization probability being constant for a given rf field.

The reasons why such high polarizations are not obtained in practice are to be found in the finite value of the electronic resonance line, the possible existence of phonon bottleneck, or of extra mechanisms of nuclear relaxation.

If $f \ll 1$, as in LMN:Nd with H greater than 1000 G, the variation of P_n with the applied rf power $\mathcal{W}$ ($s \sim W \sim H_1^2 \sim \mathcal{W}$) is given by

$$P_n = \pm P_0 s/(1 - P_0^2 + s), \qquad (3)$$

with $s = WP_0/w$, which is to be compared with the formula of Schmugge and Jeffries[5] $P_n = \pm P_0 s/[(1-P_0^2)(N_n/N_e)+s]$ corresponding to the same hypotheses. The power w necessary to obtain a given polarization P_n is, according to this last formula, N_n/N_e times greater than according to ours; this factor is 2400 in LMN:1% Nd. In order to compare those values with the experimental ones, as it is known[6] that at low temperatures a strong phonon bottleneck exists in this salt, it is worth while introducing it explicitly.

2. No "leakage"; phonon bottleneck. —It is possible to describe the relaxation of electronic spins S when there exists a phonon bottleneck for the modes M of the lattice vibrations which interact with those spins: One replaces[13] in dP_e/dt P_0 by $P = 1/(2n+1)$, where n is the num-

ber of phonons excited for each of these modes, $n = [\exp(\hbar\omega_e/kT)-1]^{-1}$ where T is the temperature of these modes, and one introduces an equation for the evolution of n. The theoretical formulas thus obtained are then in good agreement with experiments.[1,3,13]

Here we have to remark that as $\Delta\omega_e \ll \omega_n$, the electronic relaxation through forbidden transitions is induced by vibration modes M' of frequencies close to $\omega_e + \omega_n$ and $\omega_e - \omega_n$, different from the modes M which induce the allowed electronic relaxation. Those different modes have then to be introduced separately: We write $P = 1/(2n+1)$ and $P' = 1/(2n'+1)$, with $n = n(\omega_e)$ and $n' = n(\omega_e + \omega_n) = n(\omega_e - \omega_n)$. The stationary states are described by the system (II) of the equations obtained by replacing P_0 by P (P') in the terms describing the allowed (forbidden) transitions in the equations of Sec. 1, and by adding equations describing the equilibrium of modes M and M':

$$w(1-f)^2(P_e/P-1) + 4fw(P_e/P'-1)$$

$$+ 4fW(P_e \pm P_n) = 0,$$

$$4fw(1/P'-P_e)P_n + 4fW(P_n \pm P_e) = 0,$$

$$\sigma'\left(\frac{1-f}{1+f}\right)^2\left(\frac{P_e}{P}-1\right) + \frac{1}{P} - \frac{1}{P_0} = 0,$$

$$\tfrac{1}{2}\sigma'\frac{4f}{(1+f)^2}\left(\frac{P_e}{P'}-1\right) + \frac{1}{P'} - \frac{1}{P_0} = 0,$$

with $\sigma' = (N_e/N_M)wT_{ph}$, where N_M is the number of modes M, ($N_{M'} = 2N_M$); σ' is temperature independent and is related to the phonon bottleneck coefficient σ of Refs. 1 and 13 by $\sigma = \sigma'P_0$. The maximum value of P_n is given in Fig. 1 for a few values of the parameters. Let us recall that $f \sim H^{-2}$, that $N_M \sim H^2$; if $w \sim H^5$ (Kramers salts), then $\sigma' \sim H^3$ and $f\sigma' \sim H$.

If $f\sigma'P_0$ is smaller than unity, even if $\sigma'P_0$ is greater than one, it can be seen that P_n is again given by Eq. (4).

3. Application to LMN:1% Nd; comparison with experiments. —We take $H = 18\,500$ G. The value of f may be deduced from the measurements of nuclear relaxation[5] and from the atomic structure of LMN,[14] $f \cong (5$ to $8) \times 10^4/H^2$, i.e., here $(1.5$ to $2) \times 10^{-4}$. The value of σ' may be deduced from the measurements of electronic relaxation[1,3]: $\sigma' \cong (0.5$ to $1.5) \times 10^{-10}H^3$, i.e.,

here 300 to 900, so that $f\sigma'$ varies between 0.05 and 0.2.

With $T_0 = 1.12°K$, $P_0 = 0.93$; P_n^{max} as given by System II ranges between 0.79 and 0.90. The experimental values[15] vary around 0.70 and reach 0.84 in a crystal located in a "cavity" of 15 cm^3, with a Q value of 200. This maximum polarization is obtained with 1 W of power at 70 GHz, $H_1 \cong 50$ mG and, with $1/T_e = w/P_0 = 2.5 \times 10^{-18}H^5/P_0$,[3] i.e., here $1/T_e = 5 \times 10^3$, $s \cong 4 \gg s(\frac{1}{2}) \cong (1-P_0^2) \cong 0.15$.[16] With a reduced power of 10 mW, $s = 0.04$ and formula (4) gives $P_n = 0.2$, experiment 0.15.

With $T_0 = 1.4°K$, $P_0 = 0.83$, and P_n^{max} (System II) ranges between 0.68 and 0.78, to be compared to experimental values[5] 0.72, 0.66, 0.68, varying from one crystal to one another.

One may compare the power $(\sim W_0)$ which is necessary to half saturate the electronic resonance with an rf field of frequency ω_e, with the power $(\sim W_1)$ necessary to obtain half of the polarization P_n^{max}. In the first case one finds, with $\sigma' = 500$ and $P_0 = 0.83$, $W_0 T_e^* \cong 1$, where $T_e^* = \sigma' P_0^2/w$ is the electronic relaxation time measured with phonon bottleneck, whence here $W_0/w = 2.5 \times 10^{-3}$. In the second case, formula (4) gives $W_1/w \cong (1-P_0^2)/P_0 \cong 0.30$, whence $W_1/W_0 = 100$, which is to be compared to the experimental value[5] of about 130, and to the theoretical prediction of Ref. 5 which is of more than 1000. One sees that the relatively high measured value of W_1/W_0 comes, not from the fact that a high rf power is necessary to polarize the nuclei, but that one needs very little power to half saturate the electronic relaxation, because of the phonon bottleneck.

4. "Leakage"; no phonon bottleneck. – Let $(T_n')^{-1}$ be the nuclear relaxation probability due to a proper relaxation process of the nuclei, or to paramagnetic impurities S' different from the spins S. One has then to consider the nature of spin diffusion even to determine the stationary values of P_n. We suppose, for instance, that the spin diffusion is fast with respect to the nuclear relaxation which is due to their coupling with the spins S, and which acts between all the nuclei. One shows[7] that the relaxation time T_n, which is due to the spins S only and to spin diffusion, is given by

$$T_n^{-1} = (N_n/N_e)T_e^{-1}(1-P_0P_e)4f/(1+f)^2,$$

with $T_e^{-1} = wP_0^{-1}$ leading to the following in-

equality:

$$(N_n/N_e)(T_e/T_n) \le 1 - P_0P_e \le 1,$$

so that, if the measured value $(N_n/N_e)(T_e^*/T_n^*)$ where $(T_n^*)^{-1} = T_n^{-1} + (T_n')^{-1}$ is greater than this limit, there is either a very efficient "leakage" which renders T_n^* shorter than T_n, or a phonon bottleneck which renders T_e^* longer than T_e, or both.

One shows, for instance, that when the leakage is very important, i.e., $T_n^{-1} \ll (T_n')^{-1}$, the stationary value of P_n is given by

$$P_n = \pm P_0 s\{(T_n^0/T_n^*) + s[1 + (N_n/N_e)(T_e/T_n^*)]\}^{-1}$$

where T_n^0 is defined by $T_n^{-1} = (1-P_0^2)(T_n^0)^{-1}$. The usual formula

$$P_n^{max} = \pm P_0/[1 + (N_n/N_e)(T_e/T_n^*)]$$

is thus valid, but with the assumption that there exists a strong cause of nuclear relaxation different from the interaction of the nuclei with the electronic spins which are used to polarize them, and that spin diffusion is very fast.

If the leakage is due to paramagnetic impurities S', then $(T_n')^{-1}$ is proportional to $[1-(P_0')^2]$, where P_0' is the polarization of these spins, and the importance of the leakage may be reduced by increasing this polarization, i.e., by working at lower temperatures in higher fields.

In the interesting practical case of LMN:Nd, in order to calculate, for instance, the depolarizing effect of the paramagnetic centers created by the incident particle flux in a polarized target, one has to combine the treatment of Secs. 2 and 4.

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*Now at CERN, Geneva, Switzerland.

[1]P. L. Scott and C. D. Jeffries, Phys. Rev. 127, 82 (1962).

[2]R. H. Ruby, H. Benoit, and C. D. Jeffries, Phys. Rev. 127, 51 (1962).

[3]J. M. Baker and N. Ford, Phys. Rev. 136, A1692 (1964).

[4]O. S. Leifson and C. D. Jeffries, Phys. Rev. 122, 1781 (1961).

[5]T. J. Schmugge and C. D. Jeffries, Phys. Rev. 138, A1785 (1965).

[6]See, for example, C. D. Jeffries, Dynamic Nuclear Orientation (Interscience Publishers, Inc., New York, 1963).

[7]M. Borghini, to be published.

[8]A. Abragam and M. Borghini, Progress in Low Temperature Physics, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1964), Vol. 4.

[9]See, for example, A. Abragam, The Principles of Nuclear Magnetism (Clarendon Press, Oxford, England, 1961).

[10]T. J. Schmugge and C. D. Jeffries multiply the electronic relaxation through forbidden transitions by a factor N_e/N_n which renders it always negligible; they also multiply W by N_e/N_n in the equation for the evolution of P_n. This is perfectly correct when there is a fast spin diffusion, but then w must be multiplied by the same factor, which disappears from the stationary state equation.

[11]M. Borghini and A. Abragam, Helv. Phys. Acta, Suppl. 6, 143 (1960).

[12]O. Leifson and C. D. Jeffries, Phys. Rev. 122, 1781 (1961).

[13]B. W. Faughnan and M. W. P. Strandberg, J. Phys. Chem. Solids 19, 155 (1961).

[14]A. Zalkin, J. D. Forrester, and D. H. Templeton, J. Chem. Phys. 39, 2881 (1963).

[15]M. Borghini, P. Roubeau, and C. Ryter, to be published.

[16]As $f\sigma'P_0 \cong 0.1$, the solution of System II is not very different from formula (4), and we use this one for this approximate calculation.

ISOMER-SHIFT MEASUREMENT IN W^{182}

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We report here on an unambiguous Mössbauer measurement of the isomeric shift of the 2$^+$-0$^+$, 100-keV transition in W^{182}, observed between metallic tungsten and WCl$_6$. The radius of the 2$^+$ rotational state is thus different from that of the 0$^+$ ground state. Preliminary results for the isomer shifts in W^{184} and W^{186} are reported at the end of this paper. It is impossible with our present limited understanding of the electronic wave functions in W and WCl$_6$ to determine a reliable value for the difference between the ground- and excited-state radii, ΔR. An estimate of $|\Psi_s^2(0)_W - \Psi_s^2(0)_{WCl_6}|$ is presented below, from which we conclude that the mean square radius of the 2$^+$ state is greater than that of the ground state and that the value of $\Delta\langle R^2\rangle/R^2 \approx 1.3 \times 10^{-4}$. The uncertainty in this value is too great to distinguish between the value expected for a simple rotational stretching and that calculated by Udagawa and Sheline[1] in which they take account of the Coriolis antipairing effect. We present our results and analysis in the spirit of stimulating further investigations of isomer shifts between rotational states in even-even nuclei as well as encouraging additional work on electronic wave functions in the tungsten compounds.

It is well known that the rotational spectra of deformed even-even nuclei are characterized to a good approximation by a simple band structure of the form $E = \hbar^2 I(I+1)/2\mathcal{J}$. More exactly, there are deviations from this ideal rotational spectrum which become increasingly important for high-spin members of the band. It was originally suggested[2] that most of the deviations could be accounted for by a higher order term proportional to $I^2(I+1)^2$ arising from a rotational-vibrational interaction. This centrifugal stretching would also produce an increase in nuclear deformation proportional to $I(I+1)$. However, attempts to account for the deviations from an $I(I+1)$ energy spectrum by including the contributions of beta and gamma bands have met with varying success. More recently, it has been suggested[3] within the framework of a pairing model applied to deformed nuclei, that the Coriolis force should reduce the effective pairing interactions and thus increase the moments of inertia of the higher angular-momentum states. This antipairing effect would not be expected to produce a corresponding change in the deformation. Thus the knowledge of the change in deformation, together with the deviations from the $I(I+1)$ energy rule, may elucidate the roles of the various interactions.

The change in nuclear deformation may be deduced from a measurement of the Mössbauer isomer shift. The importance of such measurements has stimulated searches for a positive isomer-shift effect between rotational states with, however, little success. Fink and Kienle[4] have recently reported the observation of a small isomer shift between the 0$^+$ and first 2$^+$ states in both Gd^{156} and Gd^{158}, measured between the metal and the trivalent ion. Their