ACHIEVEMENT OF SIGNIFICANT NUCLEAR POLARIZATIONS IN SOLIDS BY OPTICAL PUMPING*

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For Tm^{169} in a crystal of 0.05% Tm^{2+} in CaF_2 we have observed a nuclear polarization $P_n = 12\%$ by using a scheme for enhancement of nuclear polarization by optical pumping in solids (ENPOPS) recently proposed in a Letter,[1] referred to as I. We have used the substance Tm^{2+}:CaF_2 to demonstrate ENPOPS for several reasons: The paramagnetic resonance,[2,3] optical absorption,[4] and crystal-field theory[5] have been studied in detail; the circular dichroism, which has been extensively measured by Anderson, Weakliem, and Sabisky[6] is so large that the Tm^{2+} spin polarization P_e can be sufficiently enhanced by pumping with circularly polarized light as to operate a microwave maser.[7] The lowest Kramers doublet ($E_{5/2}$) of the electronic ground state $^2F_{7/2}$ is represented in a magnetic field H by the spin Hamiltonian $\mathcal{H} = g\beta\vec{H}\cdot\vec{S} + A\vec{I}\cdot\vec{S}$, with $S = \frac{1}{2}$, $I(Tm^{169}) = \frac{1}{2}$, $g = 3.452$, and $A/h = -1101.4$ Mc/sec.[3] Figure 1 shows the energy levels, the populations n_i, the wave functions using as a basis the high-field eigenfunctions $|+-\rangle = |M_S = +\frac{1}{2}, M_I = -\frac{1}{2}\rangle$, etc., and the coefficient b^2, where $a^2 + b^2 = 1$. One can write the electron and nuclear polarizations as

$$P_e = (\langle S_z\rangle_{\text{th. av.}}/S) = [n_3 - n_1 + (a^2 - b^2)(n_4 - n_2)]/N, \quad (1)$$

$$P_n = (\langle I_z\rangle_{\text{th. av.}}/I) = [n_3 - n_1 - (a^2 - b^2)(n_4 - n_2)]/N, \quad (2)$$

where $N = \sum n_i$ and the subscript th. av. denotes thermal average. The electron polarization is enhanced by pumping the $4f$-$5d$ bands in the region 5400-5800 Å. As discussed in I this enhanced polarization may be transferred to the nuclei by I_+S_- relaxation or by rf saturation at ν_{24}. Only 1% of the optical decay is via the metastable state $^2F_{5/2}, E_{5/2}$ at 9000 cm^{-1} with a lifetime of 5 msec.[4] Anderson and Sabisky have observed paramagnetic resonance[8] as well as anomalous population distributions[9] in this metastable state, but with our largest optical pumping rate $U \sim 20$ sec^{-1}, we can safely assume that at low temperatures virtually all the Tm^{2+} ions are in the $^2F_{7/2}, E_{5/2}$ ground state.

Because of the wide linewidth and low concentration of Tm^{2+}, the Tm^{169} NMR is very difficult to observe, and we have used an optical method to measure both P_e and P_n, based on the differential absorption of σ^+ and σ^- circularly polarized light by the crystal using a weak monitor beam. One has

$$I^{\pm} = I_0 \exp[-l\gamma(\sigma^{\pm})] = I_0 \exp[-lf^{+}\alpha(\sigma^{\pm}, +) - lf^{-}\alpha(\sigma^{\pm}, -)],$$

where $I^{\pm}$ and I_0 are the transmitted and incident intensities of $\sigma^{\pm}$ light, l is the crystal thickness, $\alpha(\sigma^{\pm}, +)$ and f^+ are the fractional absorption coefficient and population for $M_S = +\frac{1}{2}$, and $\alpha(\sigma^{\pm}, -)$ and f^-, for $M_S = -\frac{1}{2}$. We choose to measure a circular dichroism signal

$$S = 2(I^+ - I^-)/(I^+ + I^-) = \Delta I/I_{\text{dc}} \quad (3)$$

by switching the monitor light beam rapidly between σ^+ and σ^- light. By using the result from Kramers' theorem that $\alpha(\sigma^+, +) = \alpha(\sigma^-, -)$ and $\alpha(\sigma^+, -) = \alpha(\sigma^-, +)$, and the pertinent assumptions that $S \ll 1$ and $l[\gamma(\sigma^+) - \gamma(\sigma^-)] \ll 1$, one can show that $S = KP_e$, where K is indepen-

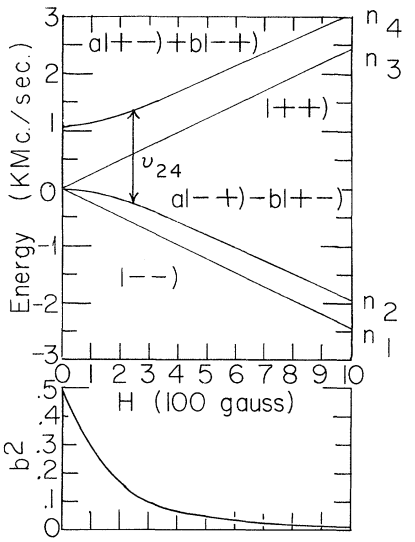

FIG. 1. Levels, populations, and wave functions for Tm^{2+}:CaF_2 as a function of H in units of 100 G.

dent of H and the temperature T and depends only on the monitor-light wavelength, the crystal thickness, and the concentration of Tm^{2+}. These are fixed for a given experiment, and K can be accurately evaluated from a measurement of $S = S_B$ with $P_e = P_{eB} = (-g\beta H/2kT)$, the spin polarization for a Boltzmann distribution in known H and T. Spectroscopy of the levels of Fig. 1 can be done easily by observing the changes in P_e and hence in S produced by inducing resonance between any pair of levels by an rf field H_1. As will be shown, the observation of S vs H is also especially convenient for the determination of cross relaxation fields when a nonthermal equilibrium population exists.

Our measurement of the nuclear polarization resulting from strong optical pumping by the main beam begins with measurement of signal S_B without pumping and S_p with pumping. From this we find

$$P_{ep} = (-g\beta H/2kT)(S_p/S_B) = P_{eB}(S_p/S_B). \quad (4)$$

We then apply a saturating rf pulse at ν_{24}, short in contrast to the optical pumping time (50 msec) and the relaxation times ($T_{1e} \sim 200$ msec, $T_{1n} \sim 1$ sec). This makes $n_2 = n_4$, leaves n_1 and n_3 undisturbed, and results in an instantaneous signal S_{pi24}. From Eqs. (1) and (2), P_n before the pulse is given by

$$P_{ni} = (-g\beta H/2kT)(2S_{pi24} - S_p)/S_B. \quad (5)$$

It should be mentioned that P_n may also be measured by combining the results of two separate pulsed saturation experiments at ν_{12} and at ν_{34}; since this method requires much longer integration times for the production of a good signal-to-noise ratio, we are unable to report meaningful results at this time. However, the signal $(2S_{pi24} - S_p)$ is much larger and we estimate that our measurements of P_{ni} from Eq. (5) are accurate to within 10%.

One of the ENPOPS schemes requires continuous saturation at ν_{24}; if S_{p24} is the steady signal observed under these conditions, then $n_2 = n_4$ and

$$P_n = (-g\beta H/2kT)(S_{p24}/S_B). \quad (6)$$

The over-all experimental arrangement is given in Fig. 2. The sample was a 5 mm × 3 mm × 1.5 mm thick crystal of CaF_2 containing ~0.05% Tm grown by the Stockbarger technique and reduced to Tm^{2+} by the Ca baking process.[10] It was mounted in a helium Dewar in the dc field of Helmholtz coils, in the H_1 field of an rf loop, and in the optical path of both the pump beam from 5400 to 5800 Å and the monitor beam at 4120 Å. Filters in the pump beam and before the photomultiplier detector provided virtually complete separation of the beams. The monitor beam was switched from σ^+ to σ^- light by a vibrating quarter-wave plate of fused silica dynamically stressed at its mechanical resonant frequency of 17 kc/sec by piezoelectric transducers. The monitor-beam optics were carefully constructed to be free of spurious circular dichroism. Steady state signals S_B, S_p, and S_{p24} were read out from the lock-in output on a chart recorder using a 1-sec integration time. For the instantaneous signal S_{pi24} following an rf pulse, a 1-msec time constant was used and consecutive signals were added in a Nuclear Data Enhancetron Model No. 1024 to improve the signal-to-noise ratio. The pulse duration was 8 msec; the pulse repetition period was 3 to 5 sec to allow for recovery of the spin system between pulses. To verify full rf saturation of the ν_{24} resonance, runs were taken with rf power an order of magnitude larger than that which produced essentially no change in S_{p24} and S_{pi24}. As a further check on the use of Eq. (5), pulsed measurements were made at thermal equilibrium and yielded $2S_{pi24} = S_B$ and $P_{ni} = 0$, as expected in the absence of optical pumping.

Figure 3 shows the electron polarization from Eq. (4) observed under strong optical pumping at $T = 1.63$°K; the Boltzmann value P_{eB} is shown for comparison. Reversing the sense of the pump circular polarizer gave essentially the same magnitude of P_{ep}, but reversed in sign,

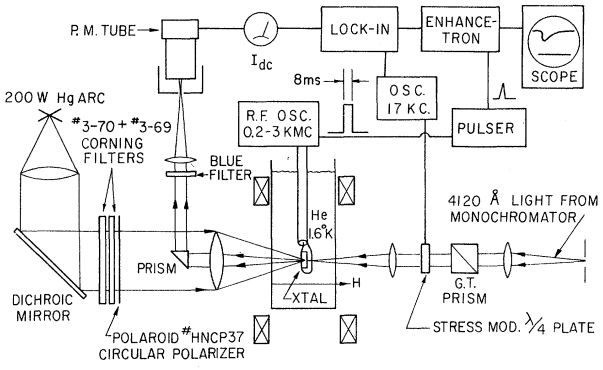

FIG. 2. Experimental arrangement for ENPOPS, showing optical system for measuring P_e and P_n.

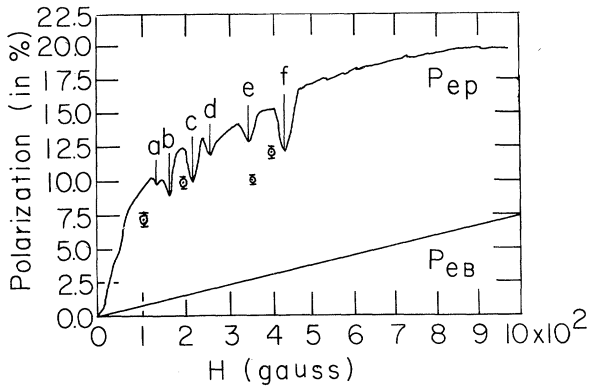

FIG. 3. Observed value of P_{ep} vs H for optical pumping of Tm^{2+}:CaF_2 at 1.63°K. The circles show measured values of P_n for Tm^{169} with optical pumping and rf saturation of ν_{24} at 1.73°K.

as expected. The dips a, b, $\cdots$ may be nicely understood in terms of cross relaxation which tends to bring various levels into spin temperature equilibrium and hence to reduce the dynamic populations. Dip b occurs where $\nu_{13} = \nu_{34}$, and dip c occurs where $\nu_{23} = \nu_{34}$; both would be effective for a pair of Tm^{2+} ions. The smaller dip a occurs where $\nu_{24} = 2\nu_{13}$ and would be effective for a triple. Dips d, e, and f occur at fields where a splitting in Fig. 1 coincides with one in the metastable state.[8,9]

We have also done many optical paramagnetic-double-resonance experiments without optical pumping by observing S vs H while applying an rf field in the range 0.2 to 3 kMc/sec. Large dips, ~10 to ~100%, were observed, corresponding to all the transitions between the four levels of Fig. 1 expect ν_{13}, which is completely forbidden. Our results agree within experimental error with the values of g and A from microwave paramagnetic resonance.[3]

Figure 3 also shows our principal experimental result: several measured values of P_n obtained from Eq. (6) by measuring S_{p24} for steady saturation of ν_{24} at $T = 1.73$°K. The largest value $P_n = 12\%$ at 395 G, corresponds to an enhancement of 605 over the thermal equilibrium value. At 395 G and 1.73°K, S_{pi24} was measured in a pulsed experiment, yielding $P_{ni} = 5.1\%$ from Eq. (5); reversing the sense of the pump polarizer gave $p_{ni} = -4.7\%$. The fact that P_{ni} is less than that obtained by steady saturation of ν_{24} indicates that the I_+S_- relaxation in the present experiment is not sufficiently strong and suggests that larger values of P_{ni} could be achieved by additional doping with an impurity which selectively cross relaxes with ν_{24}. The value of P_{ni} observed is intermediate between the values predicted in I for perfect nuclear spin memory and for randomized optical relaxation.

To summarize, these experiments are the first to demonstrate that significant nuclear polarizations can be achieved in solids by optical pumping. Results have also been obtained for protons in anthracene,[11] where the polarization mechanism is somewhat different; and for Si^{29} in silicon[12] by the scheme discussed in I; the nuclear polarizations obtained are four orders of magnitude smaller than those reported here.

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