OPERATION OF A PROTON-SPIN REFRIGERATOR*

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Using an earlier suggestion[1,2] we have achieved a polarization $p = 10.5\%$ for the protons in a crystal of yttrium ethyl sulfate $Y(C_2H_5SO_4)_3 \cdot 9H_2O$ ($YEtSO_4$) by simply rotating it in a magnetic field in a liquid-helium bath. Approximately 2% of the yttrium is replaced by paramagnetic Yb^{3+} ions, which behave like electron "spins" with a very anisotropic g factor: $g(\theta = 90°) \ll g(\theta = 0°)$, where θ is the angle between H and the crystal c axis. The Yb^{3+} spin-lattice relaxation rate is very anisotropic: $T_{1e}^{-1} \propto \sin^2\theta \cos^2\theta$. In this solid-state spin refrigerator, the Yb^{3+} spins act as a working substance, cyclically transferring heat from the protons to the bath via the crystal-lattice phonons. In the thermal block diagram of Fig. 1, heat switch S_1 can be considered closed at $\theta = 45°$ and open at $\theta = 90°$. A rapid rotation of the crystal from 45° to 90° will isentropically lower the Yb^{3+} spin temperature to $T_e = T[g(90°)/g(45°)]$. If $g(90°)$ is as small as the proton $g_n = 0.003$, rapid proton-Yb^{3+} cross relaxation closes switch S_2 at $\theta = 90°$, cooling the proton spins. After many cycles the proton polarization is enhanced by the factor $g(45°)/g_n$, yielding a polarization $p = \tanh[g(45°)\beta H/2kT]$. This method differs from classical adiabatic demagnetization in that the microscopic internal switches are automatically operated by the same external parameter θ which lowers the Yb^{3+} spin temperature. The crystal-lattice phonons are not cooled, remaining at the bath temperature T. Operation of a nuclear-spin refrigerator was first reported by Robinson[3] for anisotropic $Ce_2Mg_3(NO_3)_{12} \cdot 24H_2O$.

In our apparatus the crystal is held in a helium bath between magnet poles by a vertical motor-driven shaft. Both the c axis and the field H lie in a horizontal plane. The enhanced proton polarization is measured relative to the thermal equilibrium value $p_0 = g_n\beta H/2kT$, by means of a fixed vertical nmr coil.

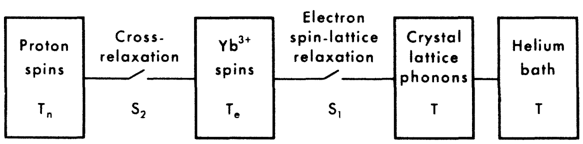

FIG. 1. Thermal block diagram for spin refrigerator.

Quantitative operation of the refrigerator clearly depends on $g(\theta)$ and the relaxation rates, which we consider in more detail. The Yb^{3+} free ion $^2F_{7/2}$ ground multiplet is split into four Kramers' doublets by the ethyl-sulfate crystal field of C_{3h} symmetry. Ytterbium-ethyl-sulfate susceptibility measurements[4,5] yield $g_\parallel = 3.40$, $g_\perp \approx 0$ for the lowest doublet. The next doublet is at $\Delta = 42$ cm^{-1}.[6] Weak microwave paramagnetic resonance has also been observed,[7] yielding $g_\parallel = 3.35$. From these data and an empirical extrapolation procedure[8] we estimate the crystal-field parameters $A_2^0\langle r^2\rangle = 140$, $A_4^0\langle r^4\rangle = -68$, $A_6^0\langle r^6\rangle = -29$, $A_6^6\langle r^6\rangle = 410$ cm^{-1}. These yield the doublet wave functions $|\pm a\rangle = |\pm\frac{3}{2}\rangle$, $|\pm b\rangle = -0.27|\pm\frac{7}{2}\rangle + 0.96|\mp\frac{5}{2}\rangle$, $|\pm c\rangle = |\mp\frac{1}{2}\rangle$, $|\pm d\rangle = 0.96|\pm\frac{7}{2}\rangle + 0.27|\mp\frac{5}{2}\rangle$; the energies are 0, 42, 133, and 263 cm^{-1}, respectively. For the lowest doublet, $|\pm a\rangle$, one calculates $g_\parallel = 3.43$, and to first order, $g_\perp = 0$. However, the field admixes $|\pm a\rangle$ with the higher doublets, giving rise to a small third-order Zeeman splitting $W = 1.5 \times 10^{-11}H^3$ Mc/sec, where H is in Oe. At $H = 17$ kOe we find $W = g_n\beta H$ so that, in effect, $g(90°) \approx g_n$; this equality is not critically dependent on H because of finite linewidths.

By a previous procedure[9,10] we calculate the Yb^{3+} spin-lattice relaxation rate

$$T_{1e}^{-1} = 1.2 \times 10^{-12}H^4T \sin^2\theta \cos^2\theta + 3.5 \times 10^{11} \times \exp(-60/T) + 1.73 \times 10^{-3}T^9 \text{ sec}^{-1},$$

the terms representing the direct, Orbach, and Raman processes. The latter two are in reasonable agreement with the measured values[5] $T_{1e}^{-1} = 5 \times 10^{11} \exp(-59/T) + 1.55 \times 10^{-2}T^9$ sec^{-1}. At lower temperatures the anisotropic direct process should dominate, giving efficient operation of switch S_1. A higher order calculation of the direct process at $\theta = 90°$ yields $T_{1e}^{-1} = 1.2 \times 10^{-35}H^8T$ sec^{-1} which, together with the Raman process, gives a negligible leakage of S_1 when it is open. Although $T_{1e}^{-1}(\theta)$ has not been observed directly, we have measured the proton relaxation rate in 2% Yb in $YEtSO_4$ at $T = 1.46°$K, $H = 10$ kOe, with the results of Fig. 2. For $0 < \theta < 85°$, T_{1n}^{-1} quali-

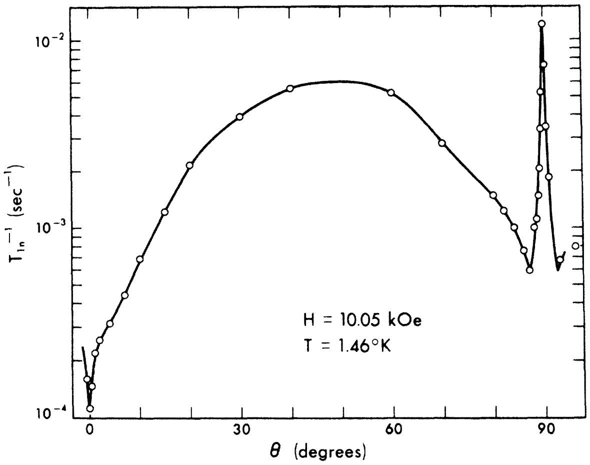

FIG. 2. Proton relaxation rate T_{1n}^{-1} vs θ in a crystal of 2% Yb in $Y(C_2H_5SO_4)_3 \cdot 9H_2O$.

tatively has the form $\sin^2\theta\cos^2\theta$. At 90° a sharp cross-relaxation spike of width $\Delta\theta \approx 1°$ is observed, as expected; this corresponds to closing switch S_2. At $\theta = 45°$, the value of T_{1n}^{-1} is reasonably close to the value 2.4×10^{-2} sec^{-1} calculated using a simple shell-of-influence model.[11,12]

Polarization experiments were performed in the field range $1.4 < H < 21$ kOe with various $YEtSO_4$ crystals containing 0.5%, 2%, and 10% Yb. In a 2% crystal, the time constant for the exponential polarization buildup varied from 100 to 10 sec as rotation speed was varied from 1 to 67 rev/sec. At constant field, the observed enhancement $E = p/p_0$ increased with rotation speed up to the highest speeds available. At constant speed, E has a broad maximum at $H \approx 10$ kOe. The largest enhancement was 165 at $T = 1.62$°K, $H = 10.05$ kOe, and rotation speed = 67 rev/sec, yielding a polarization of 10.5%. The enhancement is 4.8 times smaller than the ideal value of $g(45°)/g_n = 790$, but the nuclear polarization is an order of magnitude larger than that observed in (Ce, La)$_2Mg_3(NO_3)_{12} \cdot 24H_2O$ [3,13,14] and (Cr, Al)$_2O_3$,[15] indicating that Yb, $YEtSO_4$ is a rather favorable substance for a proton-spin refrigerator. Calculations show that less than ideal enhancement in our present experiments may be attributed to failure to switch from 45 to 90° in a time short compared to T_{1e}. At higher rotation speeds it is reasonable to expect sizable polarizations, comparable to those obtained by the dynamic microwave method.[12] The spin refrigerator is basically simpler, however, and may have advantages for polarized targets: A highly uniform field is not required; the polarization can be built up in a time ≈10 sec, and the crystal then fixed at $\theta = 0°$ where the polarization relaxes with the long time constant $T_{1n} \approx 10^4$ sec (cf. Fig. 2.)

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