

tion) postulate that another I - V break at $\sim 100I_c$ observed in some Bi samples may be the above thermal instability. However, it is this writer's opinion that this is more likely to be the film-boiling instability (see Ref. 4), since the power flux at the helium-bath-sample interface is near that required to trigger this instability. Furthermore, the calculated temperature rise at the contact, if the original size, is approximately four orders of magnitude greater than required for the present instability. In any case, it is quite ap-

parent that the original conditions no longer prevail, since the electrical conductivity is observed to increase substantially much below the I - V break, probably indicating a breakdown of the oxide layer.

⁸In unpublished data by ES (private communication) the current has been taken to about 15% of $I_c(T=0)$, somewhat below the published results.

⁹ES report (private communication) having swept through the non-Ohmic region at 10 KHz with no observed change in the behavior.

SIZABLE PROTON POLARIZATION USING A SPIN REFRIGERATOR*

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We have obtained polarization as large as 35% for the protons in a ytterbium-yttrium ethyl sulfate crystal simply by subjecting it to both dc and pulsed magnetic fields at helium temperatures. A previous paper,¹ referred to as L-J, showed that this crystal, $Y(C_2H_5SO_4)_3 \cdot 9H_2O$ ($YEtSO_4$) containing a few percent paramagnetic Yb^{3+} ions, is a favorable substance for use as a proton spin refrigerator.^{2,3} Langley⁴ has obtained polarizations up to 18% by rotating such crystals in a dc magnetic field at ~ 60 rps, which represents the practical upper limit on mechanical rotation speed because of vibration and friction. L-J predicted higher polarizations at still higher speeds, and to this end, we have constructed the apparatus of Fig. 1, in which the net magnetic field is rotated, rather than the crystal, at a frequency ~ 2 kc/sec. A $Yb:YEtSO_4$ crystal of size 8 mm \times 8 mm \times 2 mm, grown from a solution containing 2% Yb enriched to 98% Yb^{172} , is mounted in a Pyrex Dewar of He⁴ at $T \sim 1.3^\circ K$, with the crystal symmetry axis c in a vertical direction. The crystal is subject to a horizontal dc field $\vec{H}_{dc} \sim 10$ kOe from an electromagnet, and a vertical pulsed field $\vec{H}_p(t) \sim 10$ kOe, produced by discharging a capacitor through a copper solenoid, which is cooled by the liquid N_2 bath. The pulse $\vec{H}_p(t)$ has the approximate shape of a half-cosine wave with a width $\tau_p \approx 0.2 \times 10^{-3}$ sec and a variable pulse repetition period $0.05 < \tau < 2$ sec.

As discussed in L-J, Yb^{3+} ions in $YEtSO_4$ have both a very anisotropic g factor, $g \approx 3.35 \cos\theta$, and a very anisotropic direct spin-lattice relaxation rate,

$$T_{1e}^{-1} = AH^4 T \sin^2\theta \cos^2\theta, \quad (1)$$

where θ is the angle between the c axis and the total magnetic field $\vec{H}(t) = \vec{H}_{dc} + \vec{H}_p(t)$. Ideally, the spin refrigerator works as follows: If $|\vec{H}_{dc}| \approx |\vec{H}_p|$ then $\theta \approx 45^\circ$ during the pulse, so that the Yb^{3+} polarization p_e quickly relaxes to the thermal equilibrium value $p_{e0} = \tanh(g\beta H/2kT) \sim 1$, i.e., the Yb^{3+} ions become essentially completely polarized. If the pulse is switched off quickly compared to T_{1e} (which becomes much longer as $\theta \rightarrow 90^\circ$), but slowly compared to the Larmor period, then p_e retains its magnitude but adiabatically follows the net field down to \vec{H}_{dc} , where the g factor becomes comparable to the proton g factor $g_n = 0.003$. A Yb^{3+} ion can then

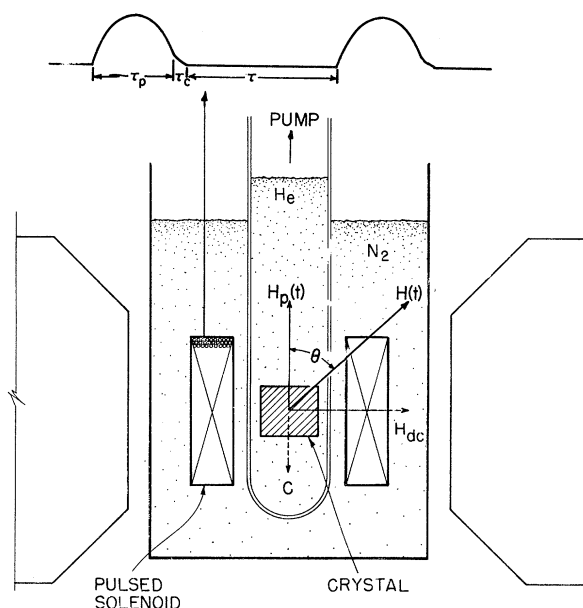


FIG. 1. Diagram of proton spin refrigerator using dc and pulsed magnetic fields.

engage in a mutual spin flip with a neighboring proton, thus aligning that proton parallel to \vec{H}_{dc} . Since the proton spin-lattice relaxation time T_{1n} is very long, $\sim 10^4$ sec, essentially all the protons in the hydrogens of the crystal will become aligned after a sequence of (N_n/N_e) pulses, where (N_n/N_e) is the abundance of protons relative to Yb^{3+} ions.

To analyze the refrigerator in more detail, we assume these coupled rate equations for the polarizations⁵:

$$\dot{p}_n = \frac{p_{n0} - p_n}{T_{1n}} + \frac{N_e}{N_n} \frac{p_e - p_n}{T_{12}}, \quad (2a)$$

$$\dot{p}_e = \frac{p_{e0} - p_e}{T_{1e}} + \frac{p_n - p_e}{T_{12}}, \quad (2b)$$

where $T_{12}^{-1}(\theta)$ is the cross-relaxation rate for mutual proton-ion spin flips; it has the form of a narrow spike of width $\Delta\theta_c \approx 1^\circ$, centered at $\theta = 90^\circ$, as observed by L-J. In principle, Eqs. (2) can be solved simultaneously for $p_n(t)$ and $p_e(t)$ if we insert the angular dependences of T_{1n} , T_{1e} , p_{e0} , and T_{12} and the function $\theta(t)$ determined empirically from $\vec{H}(t)$. However, this formidable calculation may be circumvented by the approximation of separating the cycle into three steps: polarization of the Yb^{3+} ions during the pulse τ_p ; cross relaxation of protons and ions during a time τ_c ; and spin-lattice relaxation of the protons during the time τ . In the experimental arrangement of Fig. 1 just described, it was assumed that θ becomes 90° immediately after the pulse, and that steps two and three occur simultaneously, so that $\tau_c = \tau$. However, in practice, the c axis was often set a few degrees away from vertical so that cross relaxation occurred only in the short time $\tau_c \sim \tau_p(\Delta\theta_c/45^\circ) \sim 10^{-5}$ sec during which the net field swept through the angle $\theta = 90^\circ \pm \Delta\theta_c$. The ion polarization $p_{e\perp}$ after the first step is calculated by a numerical integration of Eq. (2b), neglecting the cross-relaxation term. The result depends on H_{dc} , H_p , and the value of A in Eq. (1), which is unfortunately not yet measured, although L-J estimate it to be of order $A \sim 10^{-12} \text{ sec}^{-1} \text{ Oe}^{-4}$. For example, for $T = 1.4^\circ\text{K}$, $H_{dc} = H_p = 15 \text{ kOe}$, we calculate $p_{e\perp} = 56\%$; this value is calculated taking the initial value of p_e to be p_{e0} , since $T_{1e} \ll \tau$. In the second step we assume that the nuclear polarization, initially at p_{ni} , increases toward $p_{e\perp}$ according to the cross-re-

laxation term of Eq. (2a), so that after τ_c the nuclear polarization has increased by the amount $(N_e/N_n)(p_{e\perp} - p_{ni})f$, where $f = 1 - \exp(-\tau_c/T_{12})$. In the third step p_n relaxes for a time τ toward p_{n0} at the rate T_{1n}^{-1} . These steps can be combined into an over-all effective rate equation

$$\dot{p}_n = (p_{ss} - p_n)/\tau^*, \quad (3a)$$

$$1/\tau^* \equiv 1/T_{1n} + N_e f/N_n \tau, \quad (3b)$$

$$p_{ss} \equiv [p_{n0}/T_{1n} + (N_e f/N_n \tau)p_{e\perp}]\tau^*, \quad (3c)$$

showing that $p_n \rightarrow p_{ss}$ exponentially in a characteristic build-up time τ^* . If the pulse repetition rate $\tau^{-1} \gg N_n/(N_e T_{1n} f)$, then $p_{ss} \rightarrow p_{e\perp}$, and the build-up time $\tau^* \rightarrow \tau N_n/(N_e f)$, which can be made very short by frequent pulsing.

We have taken data for several Yb:YEtSO_4 crystals with fields in the range $2.7 < H_{dc} < 20 \text{ kOe}$, $0 < H_p < 25 \text{ kOe}$, and temperature $1.2^\circ < T < 1.6^\circ\text{K}$. The enhanced proton polarization is measured relative to the thermal equilibrium value p_{n0} by means of a vertical nuclear magnetic-resonance coil around the crystal. In all cases we observed an exponential buildup of p_n to a steady-state value. Figure 2 shows $p_{ss}|_{\text{meas}}$ versus the pulse repetition rate τ^{-1} at $T = 1.3^\circ\text{K}$, $H_{dc} = 15 \text{ kOe}$, $H_p = 15 \text{ kOe}$. The solid line is given by Eq. (3c) with the values $T_{1n} = 0.9 \times 10^4 \text{ sec}$, which is slightly shorter than the measured proton-relaxation time at $T = 1.2^\circ$, $T_{1n}|_{\text{meas}} = 1.2 \times 10^4 \text{ sec}$ at this crystal orientation ($\theta = 91^\circ$); $N_n/N_e = 1650$, calculated assuming 2% Yb; and $f = 0.22$ and $p_{e\perp} = 29\%$, required to fit the data. This value of f is consistent with the values $\tau_c \sim 10^{-5} \text{ sec}$ and $T_{12} \sim 10^{-5} \text{ sec} \approx \text{inverse proton-proton linewidth}$.

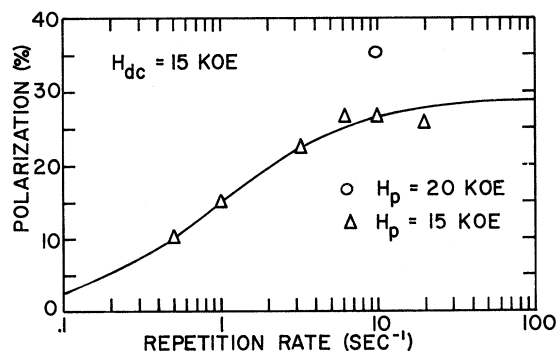


FIG. 2. Observed steady-state proton polarization versus pulse repetition rate for 2% Yb^{172} in YEtSO_4 at $T = 1.3^\circ\text{K}$. The solid line is Eq. (3c).

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 relaxation⁶ 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:YEtSO₄, 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 Yb³⁺ spin flip is important; this is the only process that could prevent the protons from acquiring the full Yb³⁺ 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 Yb³⁺ 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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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 collaborators¹⁻⁴ 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 polarization⁵ 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 Schmutge 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