DYNAMIC PROTON POLARIZATION IN BUTANOL WATER BELOW 1 K*

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We have measured the temperature dependence of the dynamic proton polarization in a 0.2-g sample of 95% 1-butanol and 5% water, containing 0.75% of the free radical porphyrexide, between 1.4 and 0.5 K. The largest polarization attained was 67% at 0.5 K. The feasibility of achieving comparable polarization in larger samples and the question of the origin of the observed temperature dependence are discussed.

The recent observation by Mango, Rundlfsson, and Borghini[1] of dynamic proton polarizations of about 40% in butanol-water mixtures near 1 K has focused attention on this material for use in nuclear scattering experiments utilizing polarized proton targets.[2] Considering the rather steep temperature dependence of the polarization $(P \sim 1/T)$ observed in this material above 1 K,[1] it has become of considerable interest to extend the polarization measurements to lower temperatures. This Letter reports the results of such measurements down to 0.5 K, carried out in a ^{3}He refrigerator[3] at a microwave frequency of 70 GHz.

The sample consisted of 0.2 g of a mixture of 95% 1-butanol and 5% water, doped with 0.75% porphyrexide[4] (all percentages by weight). Since this material has a half-life of about 12 h at room temperature, owing to the decay of the porphyrexide, it was prepared immediately prior to the experiment. After mixing, the liquid was packaged in a heat-sealed, flat rectangular bag of dimensions 7×16 mm^2, prepared from 0.025-mm fluorinated-ethylene polymer (FEP)[5] film. The sample, surrounded by the NMR coil of the Q meter used to monitor the proton polarization, was then inserted in a multimode, coin-silver microwave cavity. The cavity was cylindrical with an internal diameter of 9 mm and a height of 20 mm. No attempt was made to remove dissolved atmospheric oxygen from the sample prior to insertion in the cryostat. Rather, the sample was subjected to vacuum in the warm cryostat for two hours immediately before cool down to permit diffusion of any dissolved oxygen out through the walls of the FEP bag.

The optimal polarizations measured in ^{3}He are shown as the circles in Fig. 1. The solid squares represent measurements in a separate ^{4}He cryo-

stat on a comparable sample.

The polarization of 67% at 0.5 K is the largest proton polarization so far reported in a hydrocarbon material.[6] The large polarizations achieved at the lowest temperatures were also evidenced in the NMR derivative line shapes, some examples of which are shown in Fig. 2. The peak-to-peak linewidth at a polarization of 67% was only slightly over one-half the linewidth in thermal equilibrium at 1 K, which effect is presumably due to the increased correlation in neighboring spin directions at high polarization. The proton spin-lattice relaxation time and dynamic polarization time were not measured at the lowest temperature, but at 0.62 K they were $T_1 = 120$ min and $\tau = 17$ min, respectively. These are to be compared with $T_1 = 15$ min and $\tau = 1.3$ min at 1.0 K for the same sample.

The total microwave power dissipated (at optimal polarization settings) in the cavity plus sample was estimated from the ^{3}He boil-off rate to be
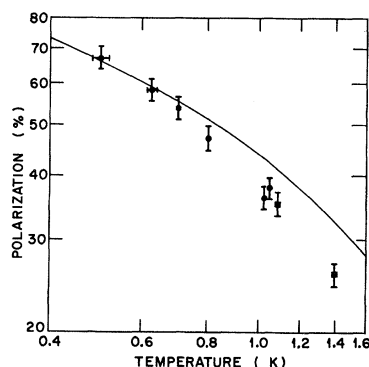

FIG. 1. Solid circles: measured dynamic proton polarization versus temperature (in ^{3}He) in 95% 1-butanol and 5% water. Solid squares: measurements on a comparable sample in ^{4}He. The solid curve is based on Eq. (1), as discussed in the text.

5 ± 1 mW at 1.0 K and 0.65 ± 0.20 mW at 0.5 K. Thus, if the power repuired scales linearly with sample mass, the total power needed at 0.5 K for a practical polarized target of 10-g mass would be about 30 mW, including power expended in the cavity walls. Since the latter is likely to be an appreciable fraction of the total power[7] and can be separately dissipated through a heat sink to the ^{4}He bath, the ^{3}He refrigeration capacity required should be within the practical range of, say, 10 mW at 0.5 K.

Since the electron thermal-equilibrium polarization at 70 GHz and 1 K is greater than 90%, the increasing dynamic proton polarization observed below 1 K probably cannot be understood in terms of a "solid effect,"[8,9] but should be explicable when electron "spin-spin effects"[10,11] are included. In particular, the "cross-relaxation" model of Ref. 11 contains implicitly a temperature dependence similar to that observed. In this model the sample average proton polarization is given by[11]

$$\langle \bar{P}(x) \rangle_{av} = \int_{-\infty}^{\infty} \frac{\{g(x-\delta)[P(x)-P(x-\delta)]-g(x+\delta)[P(x)-P(x+\delta)]\}g(x)dx}{\beta(x)+g(x-\delta)[1-P(x)P(x-\delta)]+g(x+\delta)[1-P(x)P(x+\delta)]}, \quad (1)$$

where x is a local-magnetic-field variable ($x = 0$ marks the EPR center), $g(x)$ is the normalized EPR line-shape function for the inhomogeneously broadened line, $P(x)$ is the local electron polarization, and $\beta(x) \approx [1-P(x)P_0(x)]\beta_0$ is a "leakage" parameter, $P_0(x)$ being the thermal equilibrium value of $P(x)$. In order to exemplify the temperature dependence of Eq. (1), a plausible set of parameters was first obtained by fitting Eq. (1) to the data of Ref. 1. These data consist of the proton polarization dependence on applied static magnetic field and on applied microwave power, measured at 70 GHz and 1.05 K, in a sample of 95% 1-butanol and 5% water saturated with porphyrexide.[12] Figure 3 shows these data and the best mean-square fit of Eq. (1). The EPR spectral function, $g(x)$, used in Eq. (1) was also that of Ref. 1, obtained at 70 GHz and 1.05 K. Some

extrapolation of $g(x)$ in the wings of the resonance was necessary. The parameter values corresponding to the fit displayed in Fig. 3 are[13]

$$\beta_0 = 1.7 \times (10^{-3}) \text{ Oe}^{-1},$$

$$\Omega = 99 \text{ Oe},$$

$$t = 1100 \text{ Oe}. \quad (2)$$

The temperature dependence of Eq. (1) was then evaluated by fixing the parameters at the above values and varying only the temperature [via the temperature dependence of $P_0(x)$ and $P(x)$]. The result is shown as the solid curve in Fig. 1. It is seen that, at least qualitatively, this model does yield increasing dynamic polarization below 1 K, in spite of the nearly constant equilibrium electron polarization. The increase below 1 K is
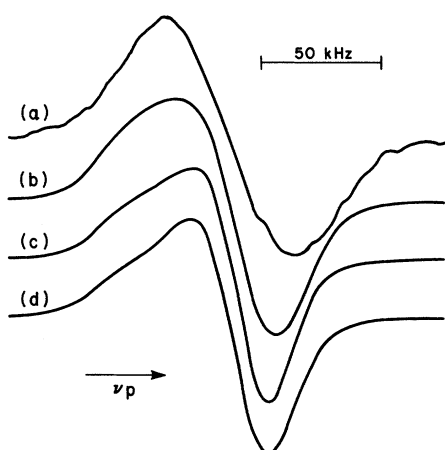

FIG. 2. The frequency-swept proton NMR derivative in 95% 1-butanol and 5% water, at polarizations of (a) 0.0026 (an average of six thermal equilibrium signals at 0.98 K), (b) 0.36 (at 1.02 K), (c) 0.54 (at 0.70 K), and (d) 0.67 (at 0.5 K). The relative gains have been adjusted to give equal signal amplitudes.
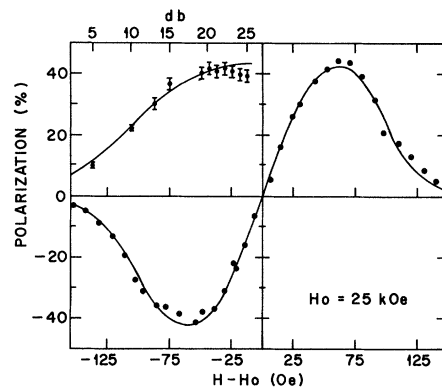

FIG. 3. The points are the data of Mango, Runólfsson, and Borghini (Ref. 1) for the dynamic proton polarization in 95% 1-butanol and 5% water, at 70 GHz and 1.05 K, versus applied static field and (in the upper left corner) versus applied microwave power. The drop in polarization at higher powers may result from microwave heating of the sample. The solid curves are derived from Eq. (1) using the parametric values listed in the text.

traceable largely to the terms second order in electron polarization in the denominator of Eq. (1). Although the model does not quantitatively fit the overall slope of the data in Fig. 1 with all parameters fixed, a 25% variation of the saturating ensemble width Ω with temperature, over the entire temperature range, would be sufficient to fit the observations. More importantly, we have not taken into account possible variation of $g(x)$ with temperature.

It should be noted that proton polarizations larger than the 67% reported here might be possible at 0.5 K, with porphyrexide concentrations other than 0.75%. However, this concentration was found to be approximately optimal at 1 K.

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[1]S. Mango, Ö. Runólfsson, and M. Borghini, to be published; M. Borghini, Bull. Am. Phys. Soc. 14, 189 (1969).

[2]A butanol-water target has recently been put into operation at 1 K at Argonne National Laboratory, and similar targets are in use at CERN and at the Stanford Linear Accelerator Center.

[3]For a description of the ^{3}He cryostat and associated superconducting solenoid, see L. R. Windmiller and J. B. Ketterson, Rev. Sci. Instr. 39, 1672 (1968).

[4]The butanol was reagent grade from J. T. Baker Company, Phillipsburg, N. J.; the porphyrexide was obtained from K and K Laboratories, Plainview, N. Y.

[5]Fluorinated-ethylene polymer, supplied by Cadillac Plastics and Chemical Company, Chicago, Ill.

[6]A polarization of 50% at 1.1 K in a 1-mg sample of ethylene glycol has been reported by H. Glättli, M. Odehnal, J. Ezratty, A. Malinovski, and A. Abragam, Phys. Letters 29A, 250 (1969).

[7]From measurements on similar hydrocarbons carried out at CERN, it has been estimated that as much as 90% of the total power goes to the cavity wall. A. Masaike, private communication.

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

[9]In the "solid effect," this behavior could be accounted for if the proton "leakage" parameter were large at 1 K and decreasing at lower temperatures. Since the (porphyrexide) electrons dominate the proton relaxation, this should not be the case.

[10]A. Abragam and M. Borghini, in Progress in Low Temperature Physics, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, The Netherlands, 1964), Vol. IV, Chap. 8; A. V. Kessenikk, A. A. Manenkov, and G. I. Pyatnitskii, Fiz. Tverd. Tela 6, 827 (1964) [translation: Soviet Phys.—Solid State 6, 641 (1964)]; M. Borghini, Phys. Letters 26A, 242 (1968).

[11]C. F. Hwang and D. A. Hill, Phys. Rev. Letters 19, 1011 (1967).

[12]Our tests show that the maximum solubility of porphyrexide in this host is 1.5% (by weight) at room temperature. That is, the saturated concentration is about twice that used in the present experiment.

[13]The parameter t is proportional to microwave power. The value listed here corresponds to 20 dB on the power scale of Fig 3. The saturating ensemble was assumed to be Gaussian in shape, as in Ref. 11, with a width of Ω.

PERSISTENT METASTABLE STATES AND THE INHIBITED SCINTILLATION OF HE II *

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The scintillation of liquid helium produced by α particles has been measured with particular emphasis on the temperature region below 1.25°K which had not been studied previously. An interpretation of the observed inhibition of the scintillation below T_λ is proposed which attributes the effect to a reduced radiative destruction rate of metastable states in He II.

Among the unusual properties of superfluid helium, which are not yet understood, is the inhibition of its scintillation[1,2] (produced by α particles) compared with that of normal-liquid helium. Experimental studies, all at temperatures above 1.25°K, of the effect on the scintillation intensity of an electric field,[3] a heat flux,[4] and rotation of the fluid[5] have failed to provide sufficient infor-

mation to establish a mechanism for the scintillation process and the inhibition effect. It has been possible to conclude only that the radiation derives in roughly equal degree from (1) the deexcitation of some sort of atomic system or exciton and (2) processes in which ion recombination plays a contributing role.

We have now extended the measurement of the