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DYNAMIC POLARIZATION OF ^{19}F IN A FLUORINATED ALCOHOL[†]

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ABSTRACT

We have studied microwave dynamic cooling of ^{19}F and ^{1}H nuclei
in mixtures of 1,1,1,3,3,3-hexafluoro-2-propanol and water, doped
with Cr(V) complex. Equal spin temperatures of the two nuclei are
produced, and the highest spin polarizations ($\sim$ 80%) are found in
mixtures near the eutectic ratio. The high fluorine content and
polarization make this a suitable material for polarized nuclear
scattering experiments.

INTRODUCTION

We recently reported[1] the first results of a program to expand
the list of nuclei with a proven capability to serve as polarized
targets, in a form suitable for intermediate energy scattering
experiments. We reported useful levels of ^{13}C-polarization in solid
samples of 99 at.%-enriched ethylene-1,2-^{13}C$_2$ glycol, polarized by
means of microwave dynamic nuclear polarization (DNP). The first
use of this material in a polarized scattering experiment was
recently completed.[2] We now report sizeable polarizations of ^{19}F
nuclei obtained by DNP in a fluorine-rich solid which can be readily
prepared.

Substantial spin polarization of ^{19}F has been attained long
ago[3,4] in some ionic solids such as CaF$_2$ and LiF. However, the
attractiveness of these crystalline materials as polarized targets
is impaired by the relative difficulty of the doping processes by
which paramagnetic centers are introduced into the solid. For prac-
tical purposes it would be preferable to be able to use the simpler
method of doping commonly applied in the case of many polarized
proton target materials, namely, dissolving a Cr(V)-complex in the
liquid phase of the material and then rapidly freezing the mixture
to form a solid solution. For this we require a material having the
following properties: a) It should be as rich as possible in the
nuclear species of interest, in this case fluorine. b) It should be
a liquid at temperatures not too far from room temperature. c) It

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should be a good solvent for the dopant, sodium bis(2-ethyl-2-hydroxybutyrato) oxochromate(V) monohydrate,[5] commonly known as EHBA-Cr(V). This complex is generally soluble only in polar solvents. d) The material should be an easy glass-former in order to facilitate the solid solution of the complex. e) For convenience, it should be readily available commercially.

After a preliminary examination of some candidate materials, most of which were fluorinated alcohols, we settled on 1,1,1,3,3,3-hexafluoro-2-propanol (HFP), which has the composition $C_3H_2F_6O$. All of the results presented below are based on this alcohol. The HFP was mainly used as received from the vendor,[6] except that it was always dried over 4A sieve[7] for a minimum of two days before use, and some isolated tests were made with re-distilled[8] HFP. The latter procedure had no apparent effect on results.

THERMAL ANALYSIS

Pure HFP is not a good glass-former, but becomes so with small admixtures of water. In such cases previous experience indicates that the best DNP results are likely to be obtained in mixtures near the eutectic composition.[9] We therefore studied samples with varying concentrations of water in HFP by means of differential scanning calorimetry (DSC).

Figure 1 shows some of the results. The scans were made at a heating rate of 2 K/min, after filling the calorimeter cup at room temperature and quenching in liquid nitrogen. From these and other scans we conclude that a eutectic exists at 6.5 - 7.5 wt.% H_2O, as evidenced by the blending of the endothermic melting features into a single low-melting feature at 230 K. The narrow exothermic peaks correspond to devitrification of the quenched glass at around 180 K. The glass transition at around 170 K is also visible as a change of specific heat. Radiation damage in a polarized target composed of this material would be expected to anneal out near this temperature.

SAMPLE PREPARATION FOR DNP

Solutions of EHBA-Cr(V) in HFP/H_2O prove to be only marginally stable at room temperature, showing a visible change of color in less than one hour. Therefore, we prepared the samples at reduced temperature, using the apparatus of Fig. 2. The apparatus consists of a circulating cold bath, a cold Pyrex mixing tube whose contents are measured by a digital balance, and a cold needle for bead formation by the standard high-voltage method.[10] Methyl alcohol is used as the bath fluid as well as the mixing tube immersant. The geometry of the tubular heat exchanger (H.E.) is compensated to eliminate, in first order, changes in buoyant force owing to any

excursions of the immersant temperature. The cold needle consists
of a stainless steel reservoir fitted with a removable hypodermic
needle, soldered to a tubular heat exchanger. The cold needle is
thermally insulated with foam rubber (not shown). Glass wool at the
bottom intercepts any stray particulates which might otherwise
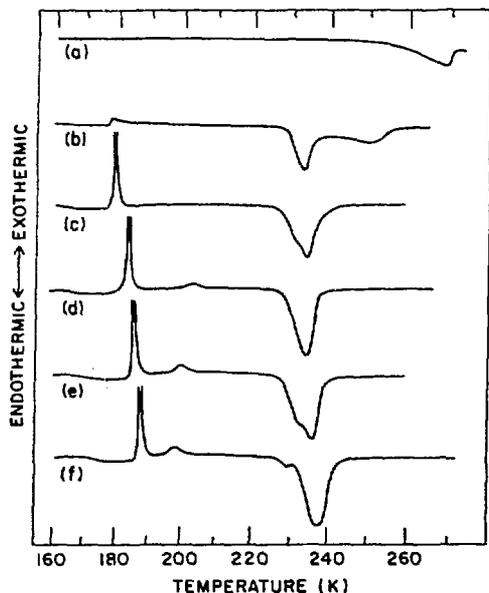obstruct the needle.

Figure 1

Differential calorimeter
scans of various mix-
tures of HFP and water.
The scans correspond to
the following percen-
tages by weight of
water: a) 0, b) 2.6, c)
5.1, d) 7.5, e) 10.1, f)
12.5. The scanning rate
is 2 K/min. Some of the
devitrification peaks
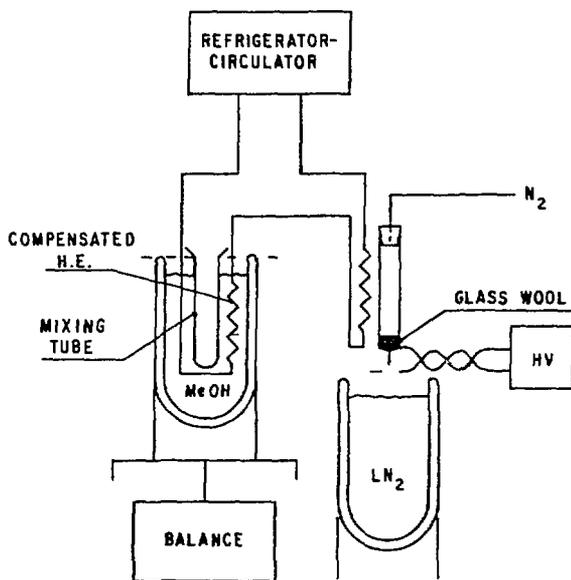have been truncated for
clarity.

Figure 2   Schematic of the sample preparation apparatus.

The sample preparation procedure was as follows: a) purge the cold needle reservoir with dry N_2, b) start circulation of coolant and wait for the temperature to stabilize at the desired preparation temperature (T_{prep}), c) weigh into the mixing tube the H_2O and HFP, d) manually mix the contents with a stirring rod (At the lower values of T_{prep}, a brief warming of 10 or 20°C, achieved by lifting the mixing tube from the coolant, was necessary in order to form the solution.), e) weigh in the dopant and stir for four minutes (Again, a brief warming was sometimes necessary to achieve complete dissolution within this time.), f) bubble N_2 through the mixture for 10 minutes in order to deplete dissolved O_2, and g) pour the mixture into the cold needle reservoir and allow the drops to freeze in the LN_2 reservoir, forming beads at a rate of about one per second. The rate of droplet formation is controlled by the N_2 pressure, and the bead diameter (1.3 - 1.7 mm) is adjusted by the level of high voltage (HV).

The total amount of mixture prepared in each case was about 3 mL. The samples for DNP consisted of 70-100 beads randomly segregated from the excess beads. The static charge on the beads was removed by means of an ionizing static eliminator.

EXPERIMENTAL METHODS

The DNP tests were done in a ^{3}He-evaporation cryostat operating at a temperature of 0.4 K in a uniform magnetic field of 2.5 T, and the hydrogen and fluorine nuclear polarization were monitored by means of NMR. The hydrogen polarization, P(H), was calibrated in the standard way by comparison to the thermal equilibrium signal obtained at 1 K. Since the cryostat structure has fluorine-containing plastic near the NMR coil, such a method could not be used for the fluorine polarization, P(F). Instead, we used the method of cross-comparing the enhanced nuclear signals at a common frequency, with a known value of P(H), as in Ref. 1. The values of P(H) were measured with an estimated uncertainty of ± 2%, and P(F), ± 4%, by these methods. In searching for the optimal sample preparation conditions, only P(H) was measured in most cases. Since, as shown below, the fluorine and hydrogen attain equal spin temperatures (EST) in these samples, the measurement of either one suffices.

The spin-lattice relaxation times of the fluorine and hydrogen nuclei, $T_1(F)$ and $T_1(H)$, respectively, were measured by timing the decay of the enhanced NMR signals after turning off the microwave field.

RESULTS

Table I shows the relaxation times and the maximum polarizations attained for the samples studied. All samples showed the highest

polarization with sinusoidal frequency modulation of the applied microwaves, with modulation rates around 2 kHz and amplitudes of 20-50 MHz peak-to-peak. The modulation typically increased the polarization by 20% for positive enhancement and 10% for negative enhancement. The optimal modulation amplitude was also about twice as large for positive as for negative.

TABLE 1

The nuclear spin-lattice relaxation times at 1 K, except as noted, and the optimal polarization achieved at 0.4 K. T_{prep} is the temperature at which the sample was mixed in liquid phase.

H_2O [wt.%]	EHBA-Cr(V) [10^{19}/mL]	T_{prep} [K]	$T_1(H)$ [min]	$T_1(F)$ [min]	P(H) [%]	P(F) [%]
6.5	3	250	2.9 ± 0.4		+75 ± 2	
6.5	4	250			+79 ± 2	
					-86 ± 2	
6.5	5	250	1.8 ± 0.1	1.8 ± 0.1	+73 ± 2	+76 ± 4
					-79 ± 2	-79 ± 4
6.5	4	240	3.0 ± 0.2		+77 ± 2	
6.5	4	270			+75 ± 2	
6.5	4	280	1.9 ± 0.1		+68 ± 2	
4.5	4	250			+72 ± 2	
7.5	4	250	2.8 ± 0.2		+80 ± 2	+76 ± 4
					-86 ± 2	-81 ± 4
			36 ± 3[a]	43 ± 3[a]		
8.5	4	240			+79 ± 2	
12.4	4	250			+73 ± 2	

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[a] At approximately 0.4 K.

The first three samples of Table I illustrate the dependence of the polarization on the Cr(V) concentration, which is optimal at 4×10^{19}/mL. The next three samples, together with the second, show the dependence on T_{prep}. The preparation must be done at temperatures below 280K; 250K seems to give sufficient stability of the Cr(V).

The last four samples, together with the second, show the dependence on water content. It is seen that the polarization peaks in the range of 6.5 - 8.5 wt.% H_2O, which is very close to the eutectic point as determined by calorimetry. As indicated above, such a relationship has been previously noticed in other materials. We believe that this phenomenon is not completely understood. To be sure, it has long been known that the glass-forming capabilities of binary mixtures are enhanced near a eutectic point;[11] the physical reasons for this are understood; and it is clear that a spatially uniform distribution of a dopant is easier to achieve in a glassy matrix than a crystalline one. However, this line of reasoning does not explain why the DNP is somewhat reduced for compositions slightly differing from the eutectic, e.g., 4.5 and 12.4 wt.% H_2O in the present case, when these compositions appear to be completely glassy both visually and calorimetrically.

Figure 3 shows the variation of the inverse spin temperatures with microwave frequency, for the sample with 7.5 wt.% H_2O. The EST condition seems to hold in this material.
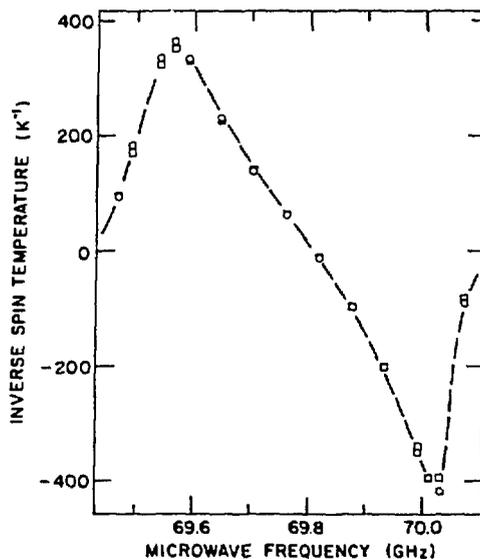

Figure 3 Inverse spin temperatures of H (circles) and F (squares) nuclei as a function of microwave frequency for the sample with 7.5 wt.% water. The dashed line is a guide for the eye.

This material polarizes fairly rapidly. For example, we measured polarizing times of about 10 minutes to reach 50% polarizations.

CONCLUSIONS

We have determined the optimum preparation conditions for a polarized target material which is rich in fluorine and can be polarized to near 80%. The material can be prepared on the "bench top" and can be handled and polarized with conventional polarized target hardware. It should be suitable for polarized nuclear scattering experiments.

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