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RADIATION DAMAGE IN POLARIZED TARGET MATERIALS*

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We examine some of the parameters which influence the decay of the polarization of polarized targets in an intense proton beam. We find that the usual characteristic flux for the polarization to drop to 1/e of its initial value does not provide a sufficient criterion to specify the radiation resistance of target materials. We give a more detailed method of evaluation including an empirical formula for the effect of annealing on the target polarization.

During the course of a recent high energy physics experient[1]) we have accumulated a significant amount of data on the radiation resistance of diol and butanol polarized targets. The experiment was performed in an external proton beam at the Z.G.S. at Argonne National Laboratory. The results allow a better comparison of the suitability of various target materials when the target must be subjected to a high intensity beam.

Diols have been used as polarized target materials because of their high proton polarization and relatively short polarizing times[2]). A diol is a hydrocarbon chain with two of the hydrogens replaced by –OH groups. The diols examined here are 1,2-ethanediol, $OHCH_2CH_2OH$, and 1,2-propanediol, $CH_3CH\ OHCH_2OH$. The target samples were prepared by mixing the diol and potassium dichromate under carefully controlled conditions of temperature, light, and pressure. The procedure was designed to give an optimum concentration of paramagnetic CrV complexes in the diol solution. Table 1 lists several properties of the diol samples: the liquid EPR derivative peak separation and the corresponding concentrations, the annealing temperatures, the nuclear relaxation times at 0.5 °K before and after irradiation, and the initial polarization values.

The target material was frozen into beads approximately 1.5 mm in diameter and placed in a 4.13 cm long by 2.89 cm diameter teflon holder. The bead filling fraction was 0.627. Inside the holder were two NMR coils for the target polarization measurement. The first or small coil was just a straight piece of 0.4 mm diameter wire with 2.5 mm o.d. teflon insulation. The second or large coil was a helix of the same wire 12 mm in diameter with 11 mm spacing between the loops. The coils were connected to separately tunable LRC series resonance circuits and were swept thru 385 kHz around the central frequency of 106.8 MHz.

The target was placed in a 25.084 kG magnetic field and maintained at 0.48 K with a ^{3}He evaporation cryostat. The polarization was dynamically enhanced at 69.30 GHz and 69.62 GHz using ~15 mW of microwave radiation. The microwaves entered at the bottom of the 4.29 cm long, 3.09 cm i.d., and 0.13 mm thick copper cavity thru a RG98/U silver waveguide.

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TABLE 1

Properties of the diol target materials.

	ΔH_c (G)	Conc.[2,15] ($\times 10^{19}$ spins/cm^3)	T_{anneal} (K)	T_{1n} (0.5 K) (min)	T_{1n}^{irr} (0.5 K) (min)	p_0 (%)
Ethanediol	5.2	8.0	160	277	220	81
Propanediol	5.4	11	180	164	141	76

After irradiation the target polarization could be partially restored by annealing the material. The heat was provided by 19 turns of enamelled 4 mil constantin wire wrapped around the microwave cavity. The heater supplied up to 35 W of power for rapid annealing. The diol samples discussed here were typically heated from 0.5 K to 160–180 K in 8–13 min.

The incident proton flux on the target was monitored with a three counter scintillation telescope. The absolute normalization was provided by calibrating the counter telescope with flux measurements from aluminum foils exposed to the incident beam. The induced β^+ activity from ^{18}F produced in the foils was counted in a calibrated NaI well counter. The horizontal and vertical profiles of the beam incident on the target were measured with segmented wire ion chambers (SWIC) located just upstream of the polarized target.

The actual measurements for one ethanediol sample are shown in fig. 1. As mentioned before, these measurements were made during the course of a high energy physics experiment. One constraint was that the average polarization be kept as high as possible and this required that we anneal the target frequently and change the target material at least once per week. As a consequence most individual measurements of the slope had rather large errors. However, many measurements were made on each sample and the resultant weighted averages are significant.

The points plotted in fig. 1 indicate the average of the readings on the large and small coils. We have only used polarization values recorded after the target had reached its maximum polarization.

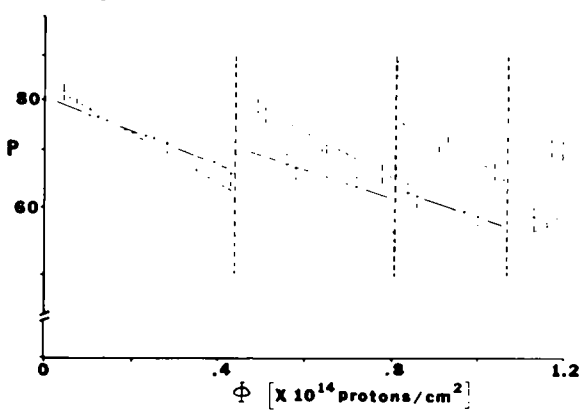

Fig. 1. The polarization of one of the ethanediol samples is shown as a function of the accumulated radiation flux. The two symbols represent positive and negative enhancements. Dotted lines indicate places where the target was annealed.

The polarizations were corrected for baseline curvature and dispersion in the NMR signal. It was difficult to keep the NMR frequency, magnetic field, microwave frequency, and microwave power simultaneously and optimally in tune, especially since the optimal parameters seemed to vary with radiation damage[3]). The parameters were retuned after each target reversal and we estimate the polarization was within 2% of maximum for most measurements. This error only applies to the upper error on the polarization. We estimate an error of $\pm 0.2\%$ on the dispersion correction, $\pm 0.5\%$ on the baseline correction and $\pm 2\%$ from beam movement. From these considerations we have assigned an error of $^{-}\frac{3}{2}\%$ to all the polarization measurements.

The number of monitor counts gives the integrated intensity, $\varphi[\#/\mathrm{cm}^2]$, of the beam striking the target. However, the relevant quantity for the abscisa in fig. 1 is the integrated beam flux, $\Phi[\#/\mathrm{cm}^2]$. We have empirically determined the flux distribution function to be

$$\Phi(x, y) = \Phi_0 \left(1 - \frac{x^2}{A^2} - \frac{y^2}{B^2}\right)^4, \tag{1}$$

where Φ_0 is the flux on the beam axis, and A and B are the semi-widths of the elliptical beam cross

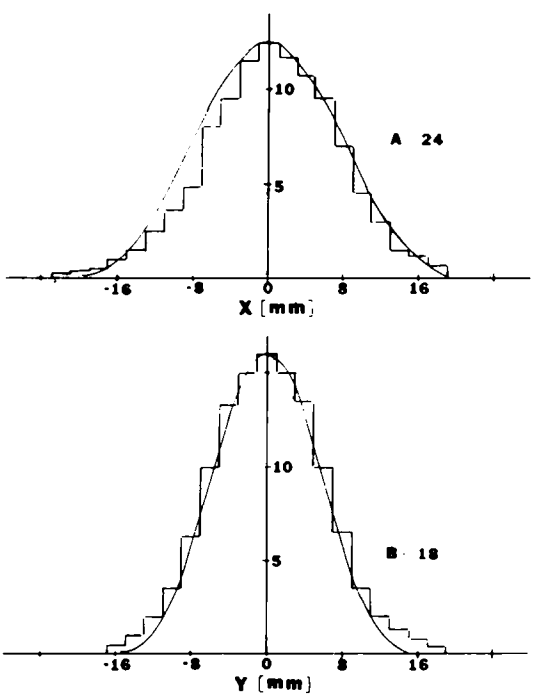

Fig. 2. The horizontal and vertical beam profiles at the polarized target. The curves indicate the integrals of eq. (1) with the given values of the parameters A and B.

section. This assumed distribution was checked by integrating eq. (1) and comparing the resultant function with the observed SWIC distributions. The agreement is satisfactory as shown in fig. 2. Integrating eq. (1) over the elliptical beam profile gives

$$\Phi_0 = \frac{5\varphi}{\pi AB}. \tag{2}$$

In principal we could use eq. (1) to compare the flux at each coil with the polarization measured there. Unfortunately the beam tended to jump around several mm on a pulse to pulse basis. This plus the inevitable problems of keeping the beam steered precisely on the target axis have prevented us from making two independent measurements. Instead we have averaged the polarization values and used the flux that is appropriate to a point midway between the coils.

We have assumed that the polarization decay followed the standard form

$$p(\Phi) = p_0\, e^{-\Phi/\Phi_A}, \tag{3}$$

where $p(\Phi)$ is the polarization after being irradiated with Φ protons/cm^2, p_0 is the starting polarization, and Φ_A is the characteristic flux[4]) for the polarization to decrease by 1/e. One iso-butanol sample was irradiated for 5×10^{14} protons/cm^2 before annealing. The sample appears to follow one exponential for the first 10^{14} protons/cm^2 and then a second less steep exponential for the next 4×10^{14} protons/cm^2. Since in practice one would not run more than 10^{14} protons/cm^2 into a target without annealing eq.(3) gives a good representation of the data.

We checked to see if there was any evidence that Φ_A was a function of the accumulated flux but found that within the errors Φ_A could be considered a constant for accumulated fluxes less than 2×10^{14} protons/cm^2. We were also unable to find any dependence of Φ_A on the instantaneous flux for fluxes $(1.0-3.0)\times10^9$ protons/cm^2·pulse.

The dotted lines in fig. 1 indicate points where the target was annealed. Qualitatively it can be seen that although the material always responded to the annealing process, it became less effective after a period of time. We present average values for the diol characteristic fluxes in table 2. The quoted errors do not include the estimated 8% uncertainty in the absolute normalization of the proton intensity measurements or 5% uncertainty in the effective beam cross. section.

It is clear from table 2 that the two enhancements damage at different rates[5]). For both diols the positive enhancement appears to suffer less anneallable radiation damage than the negative enhancement. In addition the ethanediol samples measured here appear to have significantly better radiation resistance than the propanediol. An earlier measurement[6]) of Φ_A for ethanediol at 1 K is also shown in table 2. Our results for 1,2-propanediol are lower than earlier measurements[7]) at $\frac{1}{2}$ K. This could be the result of differing concentrations and points out that to be useful radiation damage measurements should give some indication of the concentration of the irradiated material.

The fact that the polarizations shown in fig. 1 do not return to their initial values after several annealing periods shows that more than one type of damage mechanism is present. This can be seen more clearly in fig. 3 where we show the extrapolated polarization values immediately following annealing as a function of Φ for the negative enhancement data from ethanediol. The polarization following annealing steadily declines for some

TABLE 2

Radiation damage summary for diol targets.

Material	Φ_A^+ ($\times10^{14}$ p/cm^2)	Φ_A^- ($\times10^{14}$ p/cm^2)	Φ_{NA}^+ ($\times10^{14}$ p/cm^2)	$\Phi_{\bar{N}A}$ ($\times10^{14}$ p/cm^2)	p_a^+/p_0^+	p_a^-/p_0^-
Ethanediol	$2.33^{+0.32}_{-0.17}$	$1.75^{+0.18}_{-0.13}$	0.76±0.16	0.80±0.15	0.69±0.03	0.89±0.02
Propanediol	$1.24^{+0.43}_{-0.12}$	$0.94^{+0.12}_{-0.07}$	0.80±0.25	1.00±0.30	0.73±0.04	0.90±0.04
Ethanediol[6]) [+3% H_2O]	1.64±0.10	1.82±0.17				
Propanediol[7])	2.0 ±0.25	1.6 ±0.20				

characteristic amount of flux and then appears to be unaffected by further irradiation. We have parameterized this behavior with the empirical formula

$$p(\Phi) = p_a + (p_0 - p_a)\, e^{-\Phi/\Phi_{NA}}, \quad (4)$$

where p_a is the "asymptotic" polarization for large Φ, p_0 is the initial polarization, and Φ_{NA} is the characteristic flux for this non-anneallable damage to reach 1/e of its asymptotic value. We consider the ratio p_a/p_0 and the characteristic flux Φ_{NA} to be useful figures of merit when comparing the radiation resistance of target materials and show the results for both diols and both enhancements in table 2. The fluxes Φ_{NA} appear to be similar in magnitude to the Φ_A values. Also the ratio of asymptotic to initial polarizations appears to be about 70% for positive enhancement and 90% for negative enhancement for both materials.

In an effort to find a more resistant target material we have followed a suggestion by Ash[8]) and examined the isomers of butanol. The results shown in table 3 indicate that the radiation resistance for dynamic polarization is at least qualitatively proportional to the resistance to form color centers[9]). Unfortunately there may also be an inverse relation between radiation resistance and the magnitude of the polarization. The data for isobutanol also indicates that the addition of water to the sample to increase the solubility of the porphyrexide may adversely affect the radiation resistance of the sample.

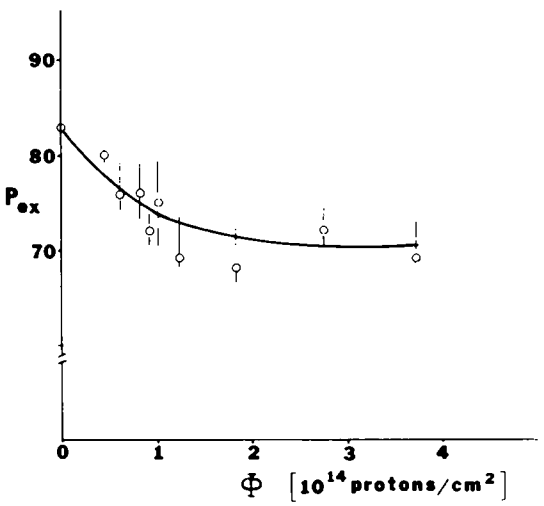

Fig. 3. The extrapolated polarization immediately following annealling is shown as a function of the accumulated radiation flux for the negative enhancement data for ethanediol. The curve is eq. (4) with the parameters given in table 2.

TABLE 3

Butanol radiation damage summary: PX = porphyrexide.

Material	Doped	p^+_{max}	p^-_{max}	Φ^+_A	Φ^-_A
n-butanol	5% H_2O 1% PX	68	−62	2.2±0.5	4.5±1.0
iso-butanol	2% H_2O 1% PX	51			
	5% H_2O 1% PX	65	−58	3.2±1.0	6.8±3.0
	8% H_2O 1.5% PX	45	−55	1.5±0.4	2.5±0.6
sec-butanol					
	5% H_2O 1% PX	62	−51	2.7±0.3	6.1±1.5
tert-butanol	5% H_2O 1% PX	~10			

It may be worthwhile to briefly review the currently accepted ideas on the mechanism of radiation damage. Irradiation of amorphous solids generally results in the partial dissociation of the solid matrix and production of trapped electrons and free radicals. Five to six paramagnetic particles are created in ethanediol for each 100 eV of absorbed dose[10]). Electrons may be trapped in inter-molecular cavities formed by groups of favorably oriented molecules. However the amplitude of the EPR line for these trapped electrons saturates and decreases at very small microwave powers[11]).

The more serious problem appears to be radical formation. Radical concentrations typically reach 10^{18}–10^{20} radicals/cm^3 in organic solids[12]). In the diols radicals are formed mainly by the elimination of an α hydrogen atom. For example $HOCH_2CHOH$ is known to be created in ethanediol and to interact via the hyperfine interaction with undamaged hydrogen atoms[13]).

Annealling is effective at depleting the trapped electron and radical concentrations. The heat provides increased molecular mobility leading to ionic recombination and reactions with molecules. In the viscous substances discussed here radical concentrations are reduced to less than 1% of the original concentration by heating to 0.6–0.7 of the melting temperature[14]). Trapped electrons are released at lower temperatures than radicals.

We have looked for some evidence of dynamic nuclear polarization from the produced radicals. Fig. 4 shows the dependence of the nuclear polarization on the microwave frequency for (1) a non-irradiated ethanediol sample, (2) an irradiated sam-

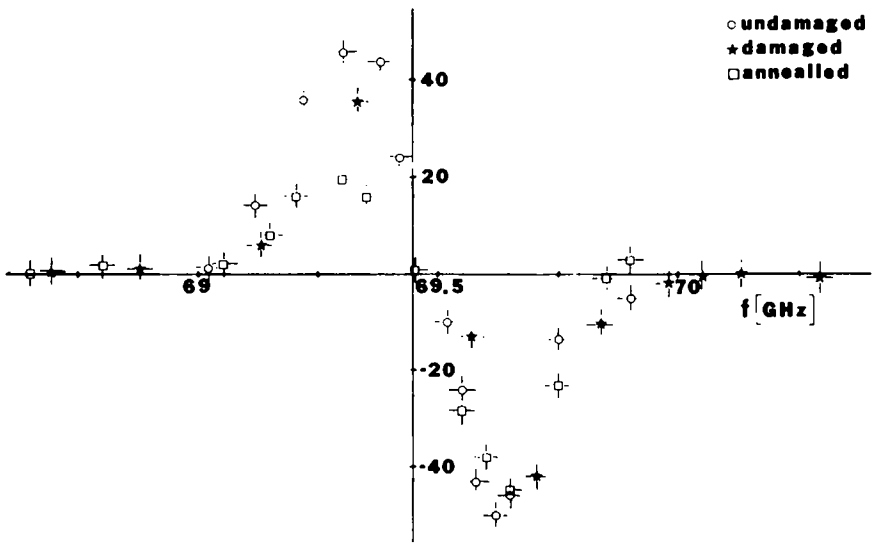

Fig. 4. The proton polarization at 0.8°K is shown as a function of the microwave frequency for a normal ethanediol sample, a damaged sample, and a damaged but annealed sample. The peaks of the damaged curve were maximized before the frequency measurements. The absolute magnitude of the normal and annealed samples are arbitrary.

ple, and (3) an irradiated sample that was annealled to 143 K. Within the uncertainty in the frequency measurement the positive enhancement (low frequency) polarization peaked in the same place for all three samples. The negative enhancement polarization for the annealled sample peaked one standard deviation higher than the normal sample, while the damaged sample peaked three standard deviations higher. However there was no evidence of any induced polarization greater than 2% in the tails of the diol signal and in particular near 70.17 GHz which corresponds to $g = 2$.

The shifting of the diol negative enhancement peak and the values for Φ_A in tables 2 and 3 suggest the following qualitative scheme for the effect of radiation on dynamic polarization. First the radiation may reduce the polarization of both enhancements roughly equally by creating molecular fragments, liberated hydrogen, etc. which can interact with the proton spin system and short-circuit the dynamic electron-proton spin-spin coupling. This could cause the observed shorter relaxation times in the damaged samples. Secondly, free radicals and trapped electrons (which are produced with $g \approx 2$) could modify and broaden the EPR spectrum of the CrV. These new paramagnetic entities would have the greatest effect on the negative enhancement of the diols and positive enhancement of the forms of butanol. Examination of tables 2 and 3 shows that $\Phi_A^- < \Phi_A^+$ for the diols and $\Phi_A^+ < \Phi_A^-$ for all the isomers of butanol. In addition as mentioned above the radicals can be largely removed by annealling.

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[3] The microwave frequency for maximum polarization in the negative enhancement appeared to shift to higher frequencies as the samples became damaged. There was no apparent shift in the positive enhancement frequency.

[4] We use the subscript A to indicate that on a short term basis most of this damage could be annealled away.

[5] We define positive enhancement to be in the same direction as the thermal equilibrium signal.

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