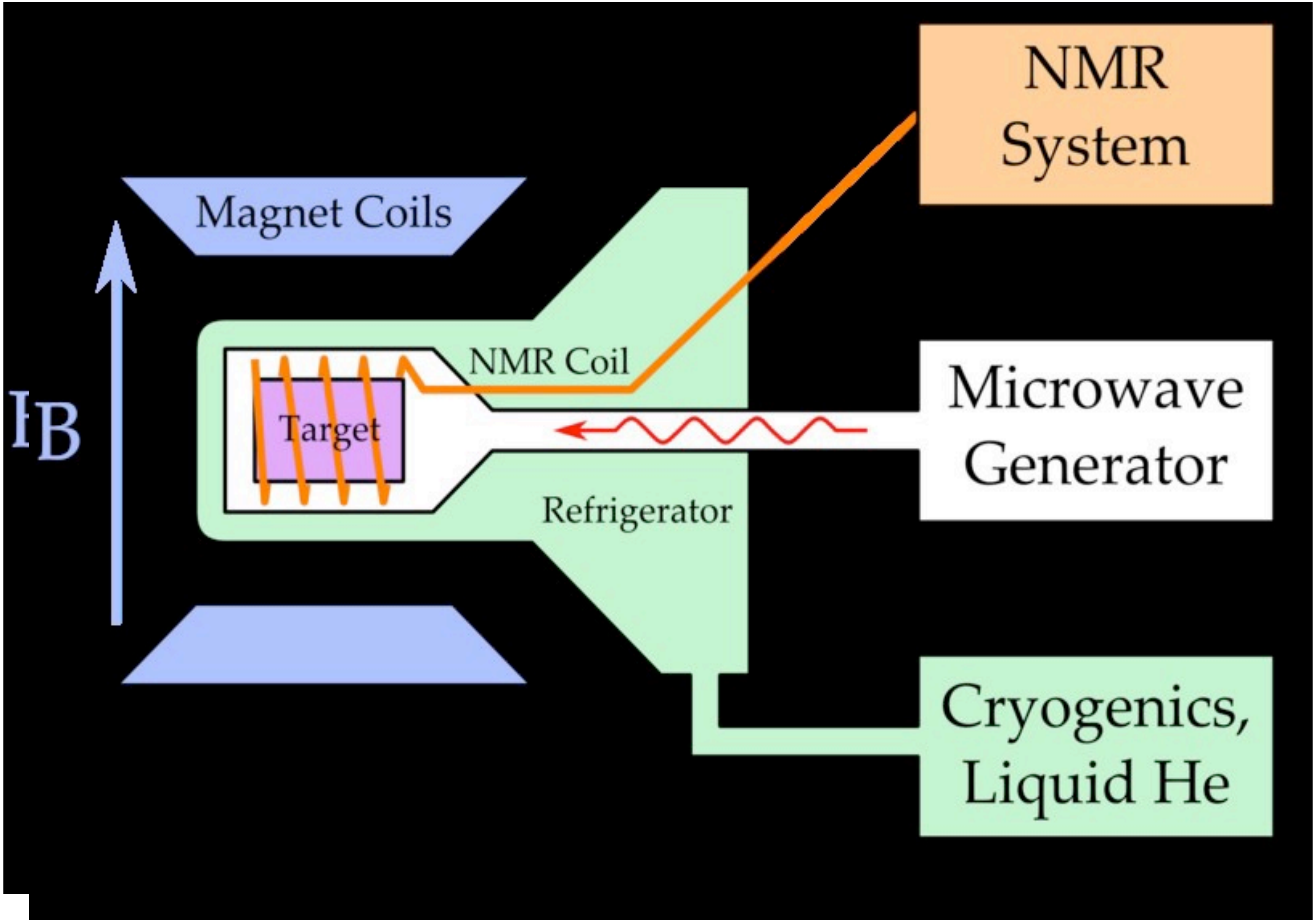
Fifty Years of Polarized Targets

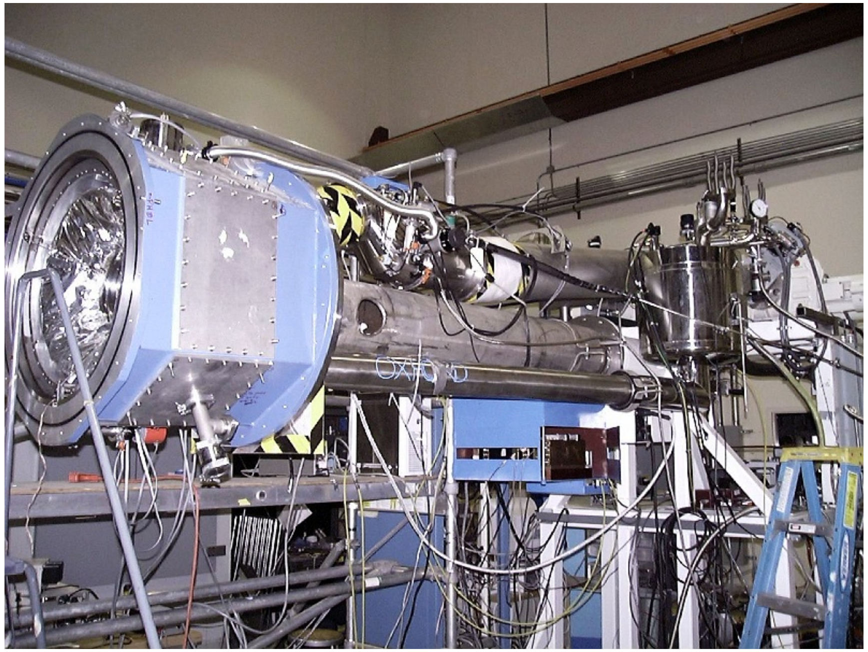
A personal Memoir

D. G. Crabb
University of Virginia

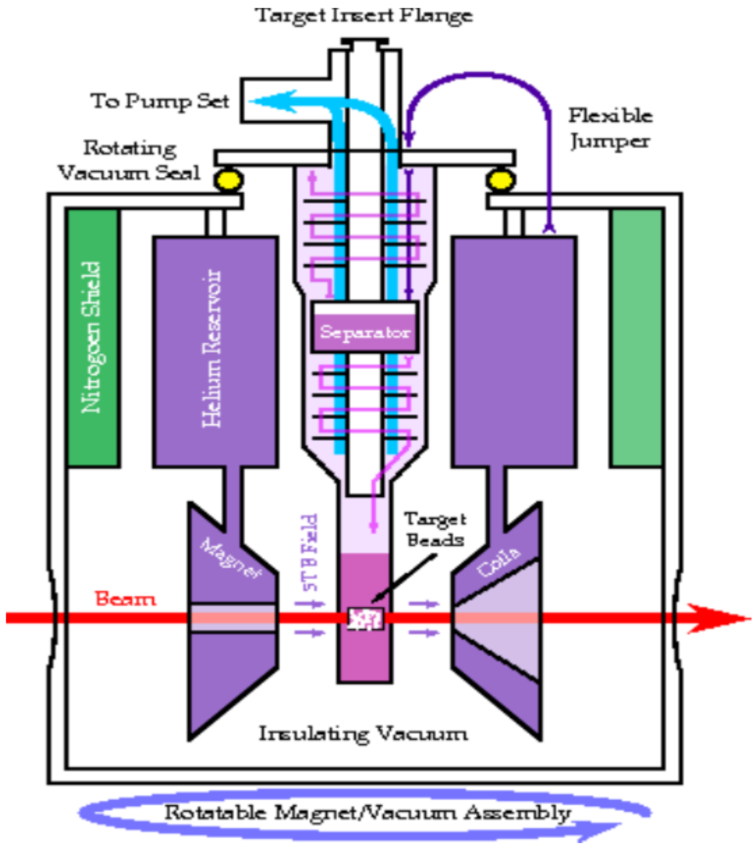


NMR System
Magnet Coils
NMR Coil
Target
B
Microwave Generator
Refrigerator
Cryogenics, Liquid He

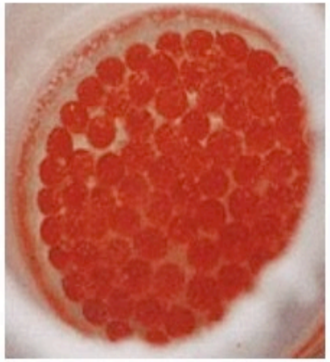
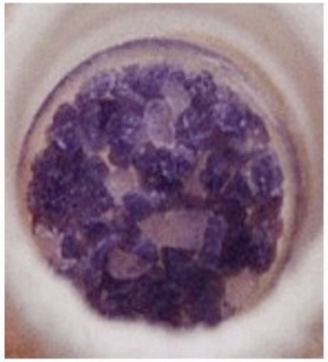
What is a (*Solid*) Polarized Target



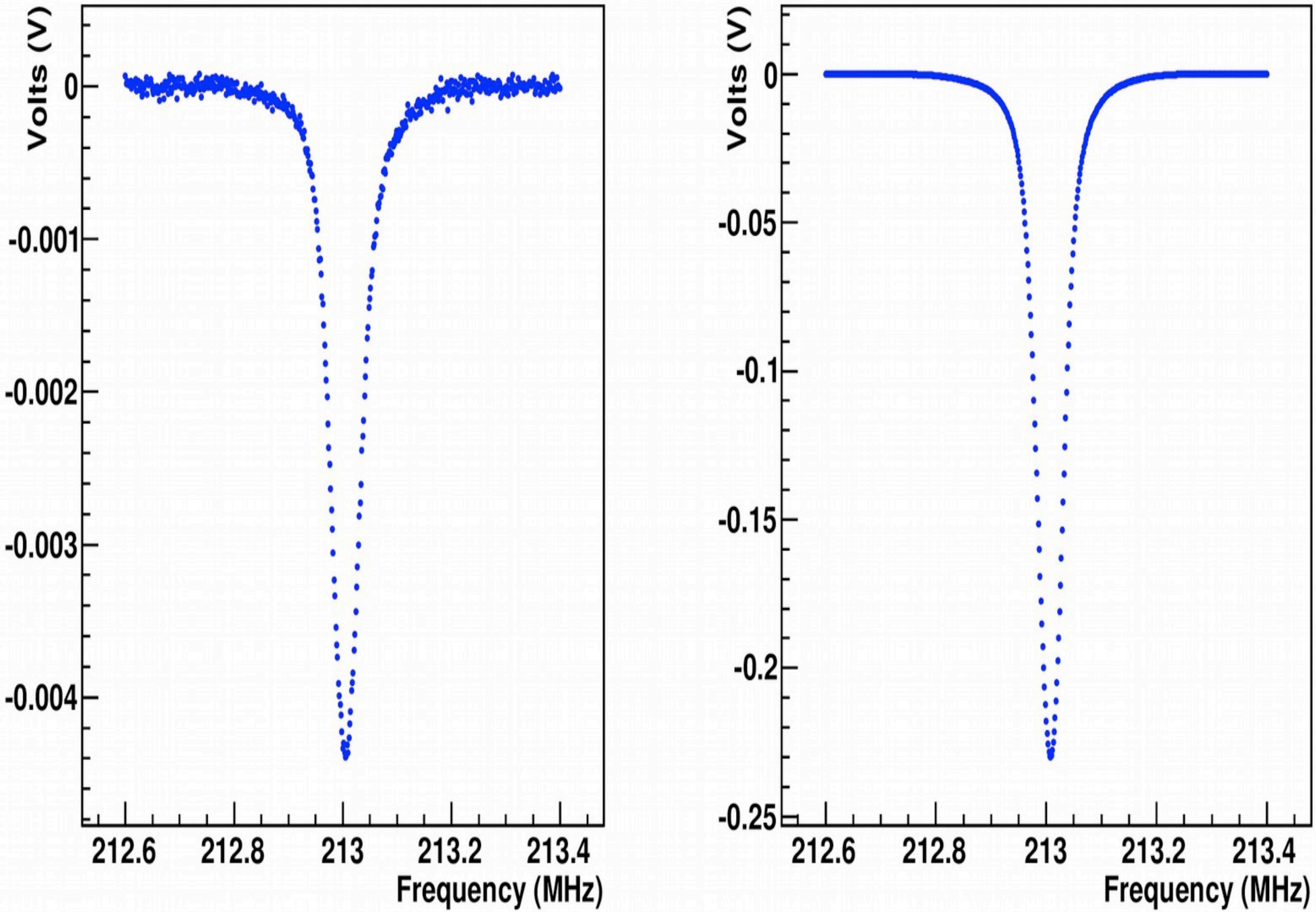
- Magnet ~2 T → ~7 T
- Refrigerator ~ 50 mK → ~ 1K
- Microwaves ~ 50 GHz → 220 GHz
- Carcinotron, Klystron, EIO
- Target Material Butanol, Ammonia, Lithium Hydride
- Chemically or irradiation
- doped.
- NMR Liverpool system

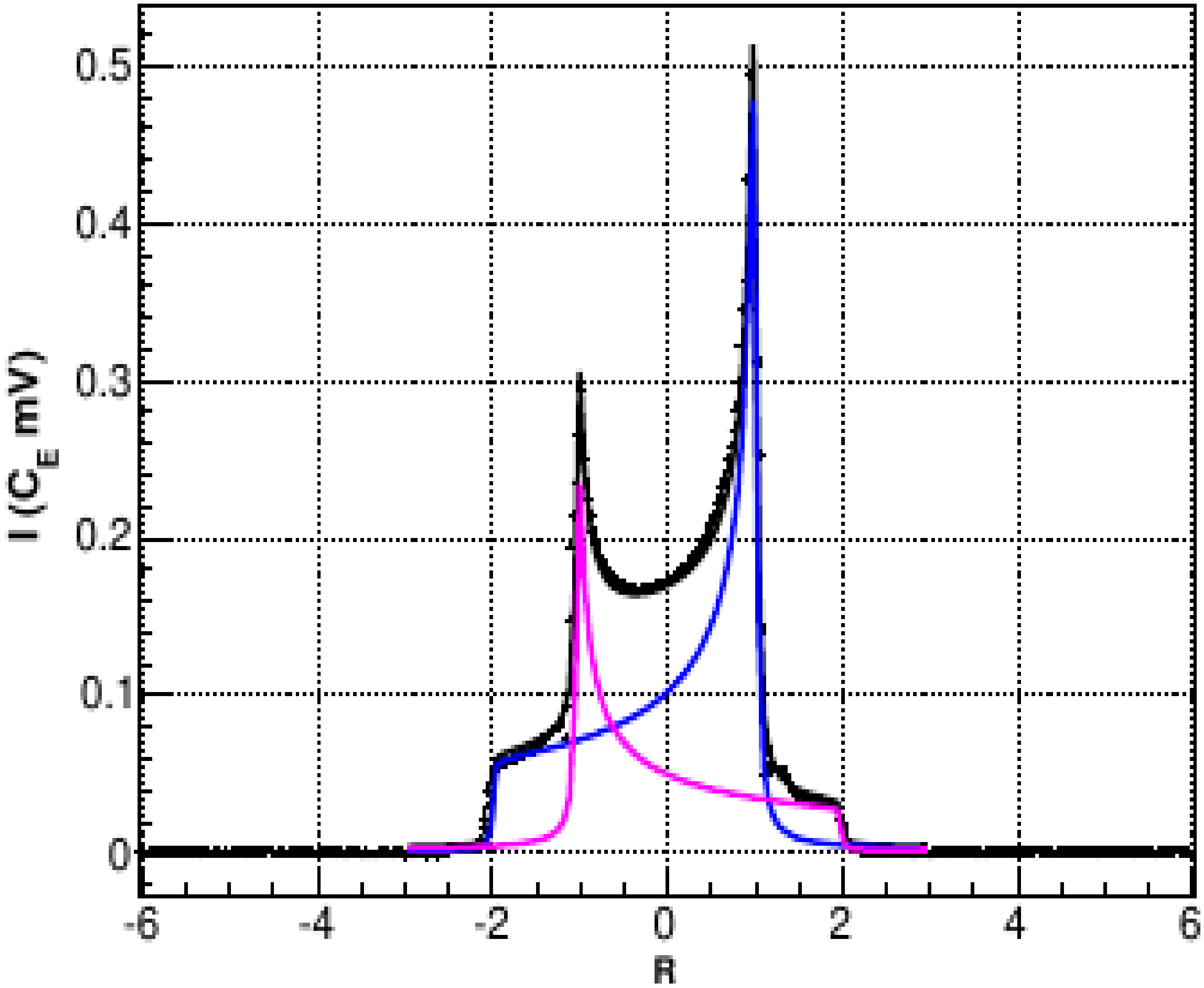


- Successful material for DNP characterized by three measures:
  1. Maximum polarization
  2. Dilution factor
  3. Resistance to ionizing radiation

Material	Butanol	Ammonia, NH_3	Lithium Hydride, ^7LiH
Dopant	Chemical	Irradiation	Irradiation
Dil. Factor (%)	13.5	17.6	25.0
Polarization (%)	90-95	90-95	90
Material	D-Butanol	D-Ammonia, ND_3	Lithium Deuteride, ^6LiH
Dil. Factor (%)	23.8	30.0	50.0
Polarization (%)	40	50	55
Rad. Resistance	moderate	high	very high
Comments	*Easy to produce and handle*	*Works well at 5T/1K*	*Slow polarization, but long T_1*


Volts (V)
0
-0.001
-0.002
-0.003
-0.004
212.6
212.8
213
213.2
213.4
Frequency (MHz)
Volts (V)
0
-0.05
-0.1
-0.15
-0.2
-0.25
212.6
212.8
213
213.2
213.4
Frequency (MHz)


I (C_E mV)
0.5
0.4
0.3
0.2
0.1
0
-6
-4
-2
0
2
4
6
R

Giants of Polarized Targets

A. Abragam

First Polarized Target

Solid theory

Dispute with Borghini over EST

VS

M. Borghini

Student of Abragam

Devised Equal Spin Temperature Theory

Conflict with Abragam

FICHE D'ACHEMINEMENT - ROUTE SLIP

A :
TO : DONALD CRABB

Veuillez/Please

- [x] Donner suite/Take action
- [ ] Approuver/Approve
- [ ] Commenter/Comment
- [ ] Signer/Sign
- [ ] Noter/Note
- [ ] Payer/Pay
- [ ] Classer/File
- [ ] Retourner/Return

P(H) and P(D) are implicitely related by

$$P_H = \tanh \frac{h f_H}{2kT}$$

$$P_D = \frac{4 \tanh \frac{h f_D}{2kT}}{3 + \tanh^2 \frac{h f_D}{2kT}}$$

T : spin temperature, is a parameter (varying around a few millidegrees)

h = Planck's constant
k = Boltzmann "
f_H = proton Larmor frequency (106.5 MHz)
f_D = deuteron " " (16.5 ")

SIS/RD/53

De
From: M Borghini

No. Tel. 3428

Date 26.1.77

First Polarized Targets

- Abragam (Saclay) and Jeffries (Berkeley) ~ 1962

  $La_2Mg_3(NO_3)_{12} \cdot 24H_2O$ doped with Neodymium

  Polarizations ~ 70% at ~1K and 2.0 T

  Borghini (CERN) ~1969

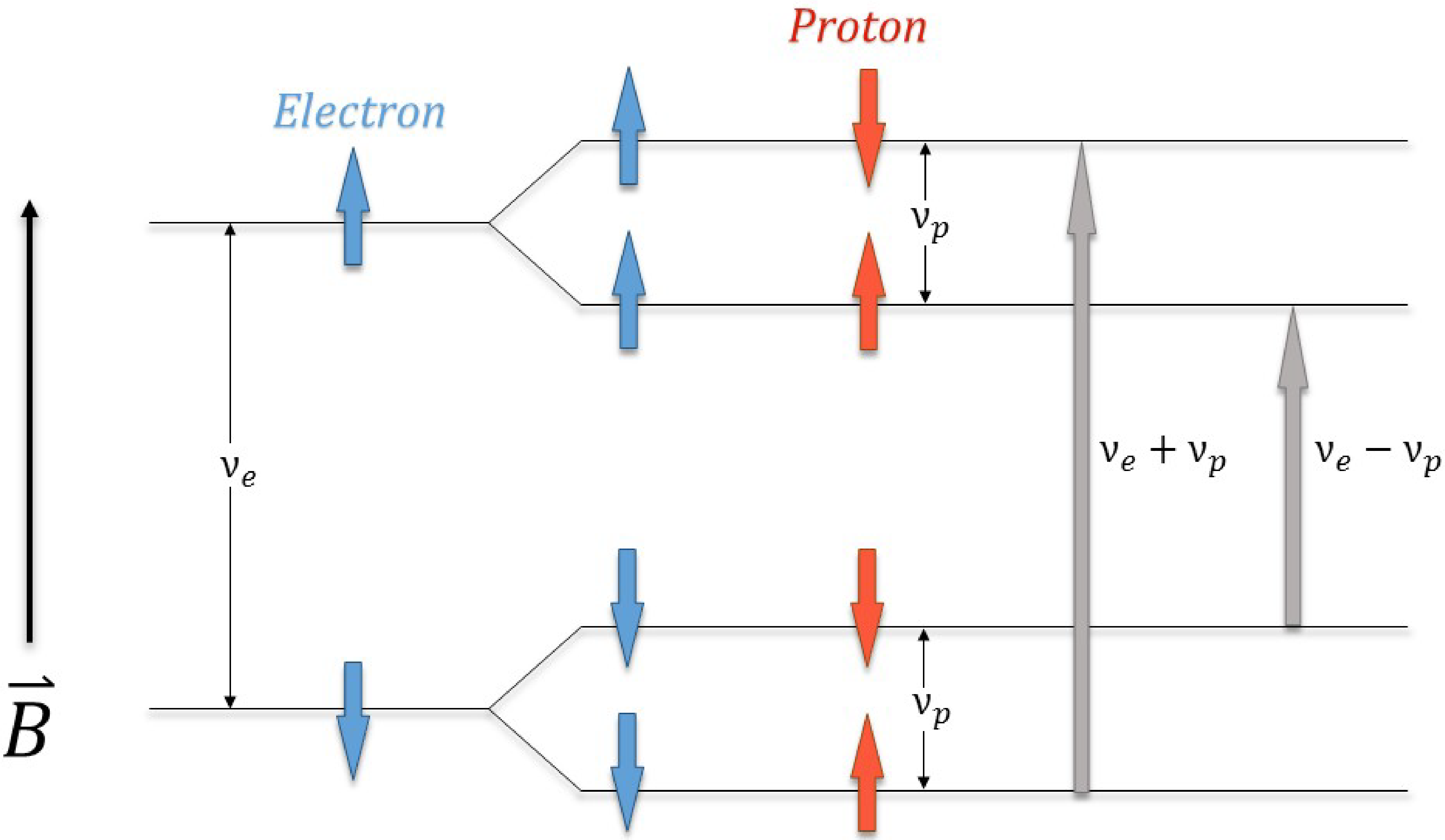
  Butanol, Diols doped with porphyrexide, CrV etc

  Polarizations 70 % - 80% at 0-.5K and 2.5 T

  Niinikoski (CERN) and Crabb (Michigan) ~1980

  NH_3

  Polarizations ~ 95% 0.3K, 2.5T and 1K , 5T



Proton
Electron
ν_p
ν_e
$\nu_e + \nu_p$
$\nu_e - \nu_p$
ν_p
$\vec{B}$

Simple Brute Force Polarization

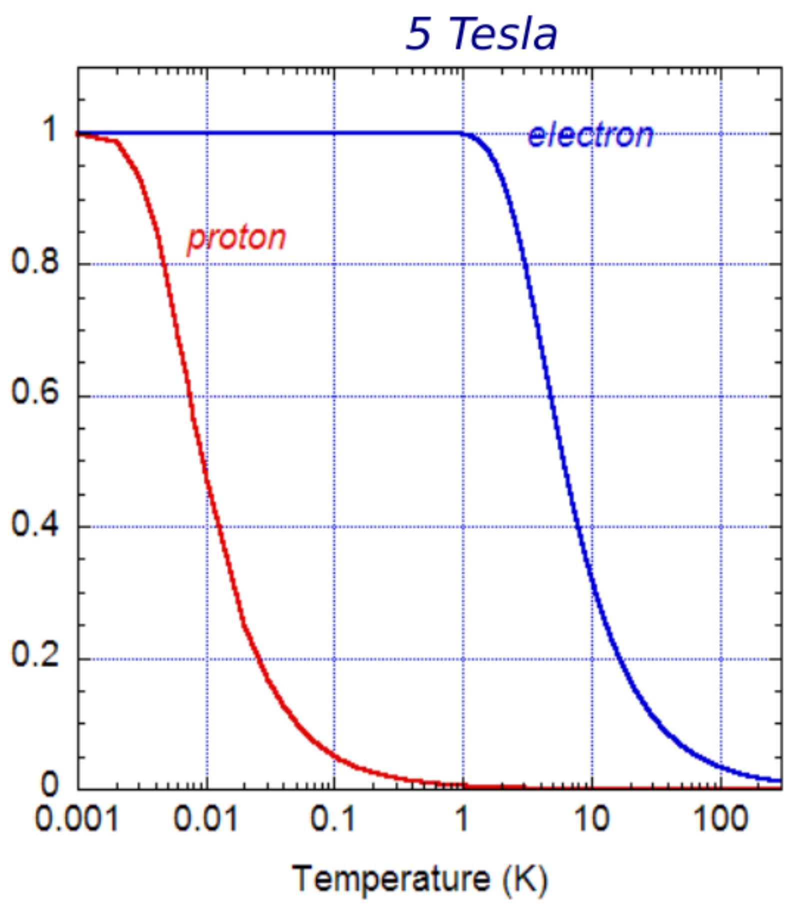
Advantage:

- Works for almost any material
- Easy to explain

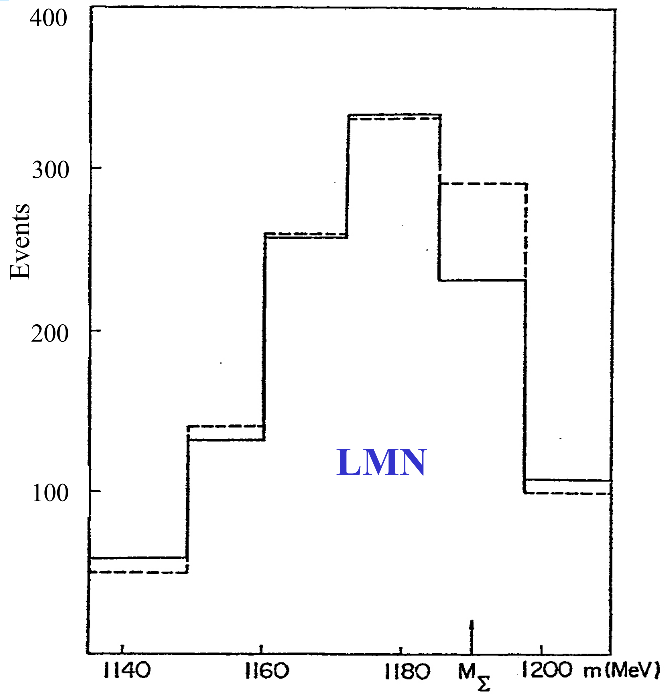
Disadvantages:

- Requires large magnet
- Low temperatures mean LOW luminosity
- Polarization can take a very long time (long T_1)

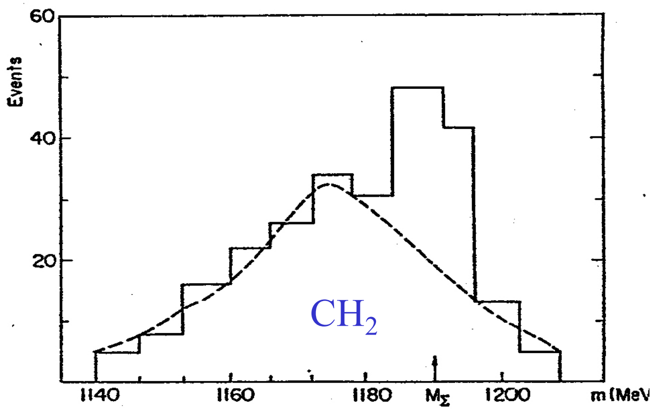
$$P_{TE} = \frac{e^{\frac{\mu B}{kT}} - e^{\frac{-\mu B}{kT}}}{e^{\frac{\mu B}{kT}} + e^{\frac{-\mu B}{kT}}} = \tanh\left(\frac{\mu B}{kT}\right)$$



Comparison of the data with LMN and CH_2 in $\pi^+ + p \rightarrow K^+ + \Sigma^+$ Reactions*



(a)

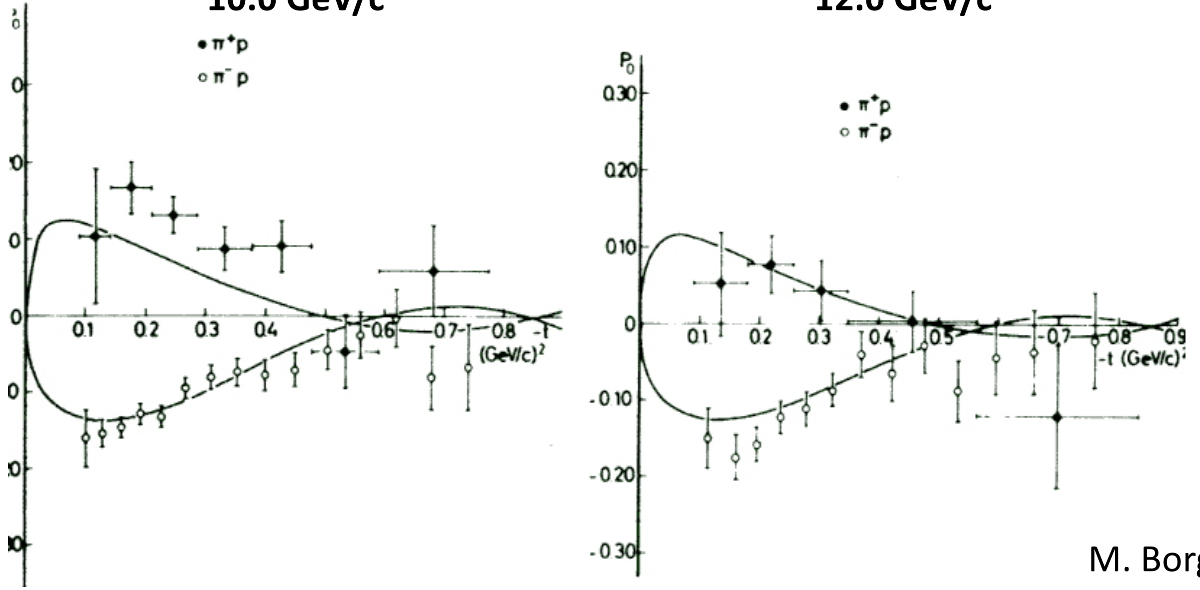


(b)

- Although LMN was an excellent polarized target material for elastic scattering experiments, it was not convenient for other experiments, e.g. backward scatterings, inelastic scatterings, rare decays, and for electron and photon beams.
- In the experiment of $\pi^+ + p \rightarrow K^+ + \Sigma^+$ reaction which was tried to carry out in CERN and Berkeley (1964) in order to check the parity conservation.*
- It was difficult to find the true events because of background events from other nuclei than free protons, since the ratio of free protons to bound protons is 1 : 15.

Asymmetries of Pion-Proton Elastic Scattering

10.0 GeV/c **12.0 GeV/c**



M. Borghini et.al

- LMN targets were successfully operated for elastic scattering experiments with π, K, p and n beams, and became important tools for particle physics.
- LMN targets were constructed in Berkeley, Saclay, CERN, Argonne, Rutherford, Brookhaven, Nagoya, INS, Liverpool, Los Alamos, Harvard, Dubna, Protvino etc. (most of the high energy laboratories in the world)
- Not in SLAC and DESY because of radiation damage with electrons.

2^{nd} Generation Polarized Target

Breakthrough in 1969

- Protons in **butanol** with small amount of water doped with **porphyrexide** were polarized up to 40 % at 1 K and 2.5 T at CERN by S.Mango, O.Runolfsson and M. Borghini, .

- At the same time, protons in **diol solutions with Cr^{5+} complex** were polarized up to 45 % at 1 K and 2.5 T at Saclay by M. Odehnel and H. Glättli.

Test of Polarization in Organic Materials in late 1960s

- Dynamic polarizations had been tested with organic materials with free radicals in many laboratories in the last half of 1960s, since these materials have higher concentration of free protons, and are strong for radiation damage.
- LMN and diol are damaged with relativistic particles of $2 \times 10^{12}/cm^2$ and $5 \times 10^{14}/cm^2$, respectively.
- At CERN more than 200 materials with more than 500 mixing ratios had been tested to polarize with several kinds of free radicals.
- However, most of them could not be polarized more than 30 %.*

Materials tried to polarize at CERN (in 1965 ~ 1971)

by M. Borghini, S. Mango, O. Runolfsson,
K. Sheffler, A. Masaike, F. Udo

Benzene
Toluene
Ethanol
Methanol
Propanol
Polyethylene
Polystyrene
LiF
Wax
Para Wax

Polexiglass
M-xylol
Mylar
$C_6H_5CF_3$
Diethylether
Tetracosane
Octacosane
$LiBH_4$
Cyclododecan

Palmitin acid
Polyphene
Thanol
Prophlbenzol
Phenylethylether
Phenylethyl-alcohol
$NaBH_4$
Prehnitene
Durol

Anthracene
Hexanol
Water
Propanol
Methylcyclohexan
Isodurol
Tetrahydrofuran
O-xylol
2,5 Dimethyltetrahydrofuran
1-Hexadecarol
Dioxan
Oppanol
$(CH_3)_4NBH_4$
$(CH_3CH_2)_4NBH_4$
NH_4BH_4
Tetramethylbenzene
Tritetra-butylphenol

Benzen + Ether
Propanol + Ethanol
Ethanol + Water
Ethanol + Methanol
Ethanol + Propanol
Ethanol + Diethylether
Butylalcohol + Methanol
Methanol + Propanol
$NaBH_4 + NH_4F + NH_3$

Free Radicals

DPPH
PAC
BPA
Shape BPA
Violanthrene
Porphyrexide
TEMPO
Ziegler
Anthracene Na^+
TMR
PB
PR
TMPD
Tri-tetra-bythlphenyl
Tetramethyl 1,3 cyclobutadien
DTBM
etc.

BPA + DPPH
BPA + Cob. Oleale
Ziegler + DPPH
Ziegler + Cob. Oleale
Ziegler + BPA
etc.

- **neutron irradiation**
- **^{60}Co-γirradiation**
- **γ- irradiation**
- **e- irradiation**

- Further Improvements

- Borghini (CERN)

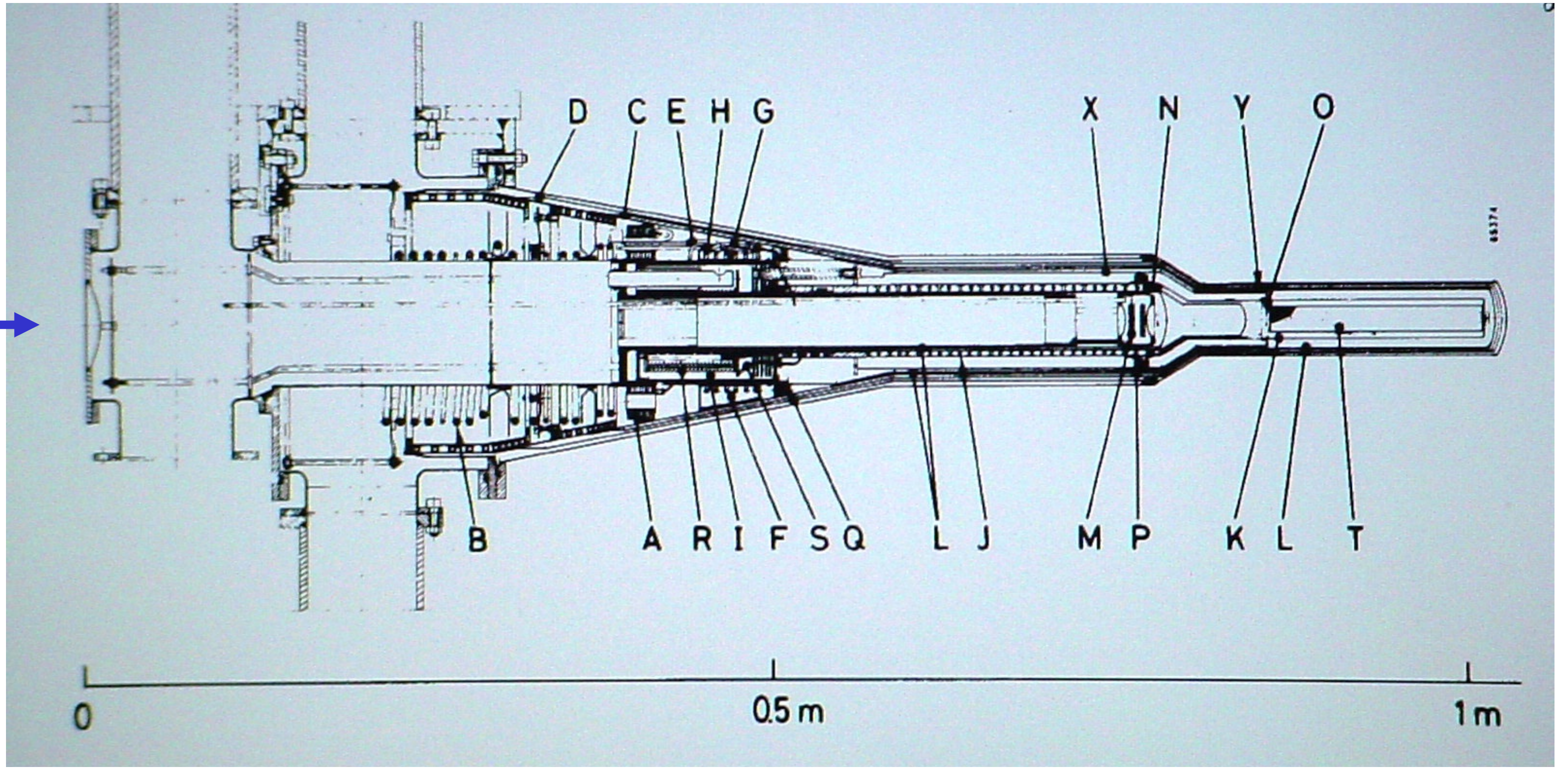
^{3}He (~ 0.5K) and dilution (<< 0.5K) refrigerators at 2.5 T

Diols and butanol polarized up to ~90% with eg. CrV dopant

Radiation Damage resistant materials

• Spin frozen targets with dilution refrigerators were constructed at **CERN and KEK in 1974**, then Saclay, Dubna and Bonn a few years later.

Beam



The Dilution Refrigerator for Spin Frozen Target at CERN

T. Niinikoski

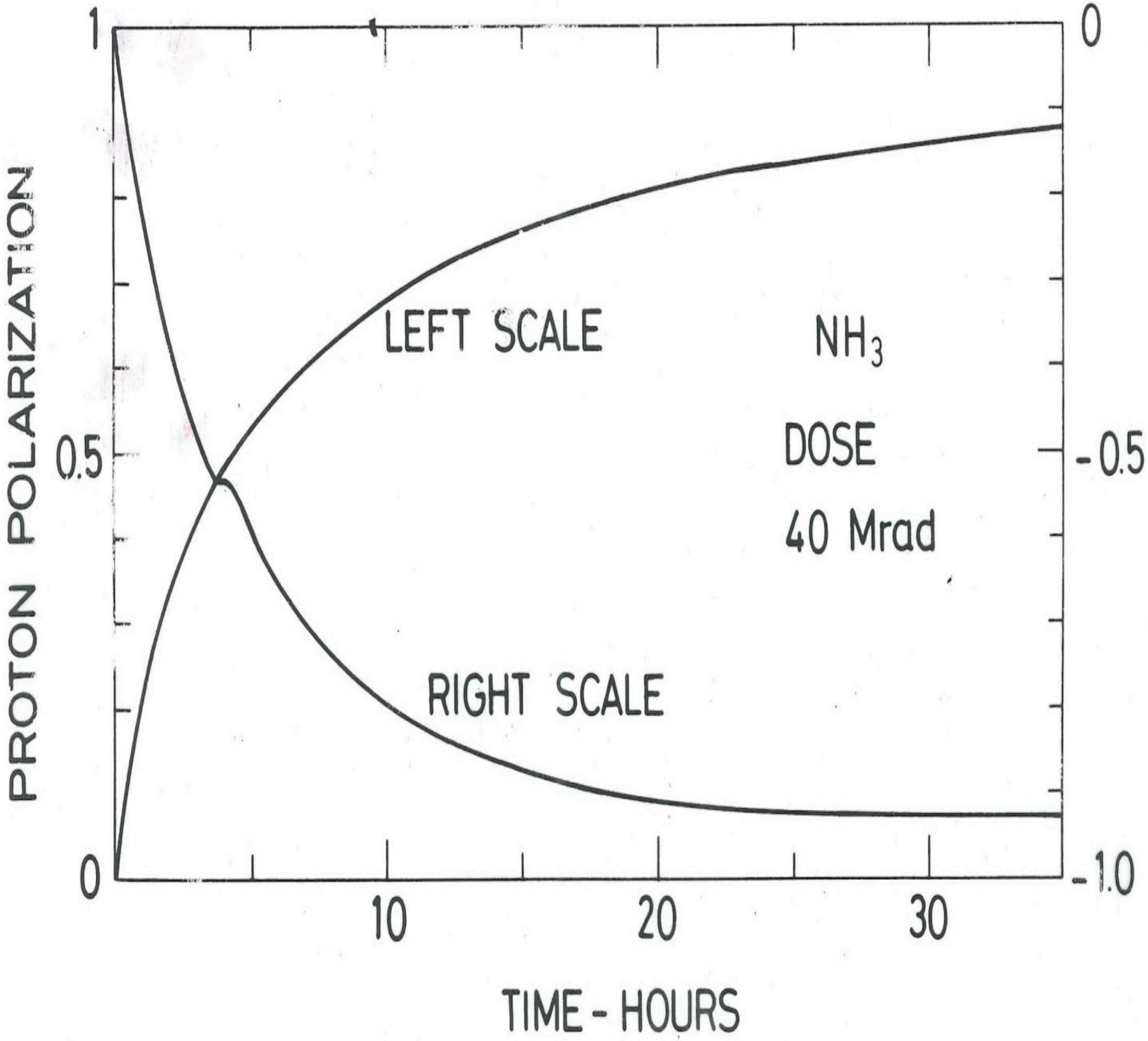
T < 50 mK   B = 2.5 T

Propanediol polarization : 80 ~ 90 %

• Beams pass through the central axis of the cryostat.

Radiation Doping

- Suggested in early 1960s that radiation damage centers (free radicals) could be used to produce polarization in suitable hydrogenous materials. Comment by H. Atkinson (RL) “that it should be possible to polarize burnt toast as it was known to contain radicals!”
- Various attempts to irradiate and polarize CH_2 : Chester Hwang at North Western U. Reached 10% at 1.2 K and 2.5 T.
- Because of the success of Borghini’s EST scheme, idea abandoned until late 70s
- 1980 Workshop on Polarized Materials Rutherford Lab Report RL-80-080 showed that NH_3 could be polarized to >90%, by Niinikoski et al and that LiH (Abragam et al) could be as well.


PROTON POLARIZATION
1
0.5
0
0
-0.5
-1.0
10
20
30
TIME - HOURS
LEFT SCALE
RIGHT SCALE
NH3
DOSE
40 Mrad

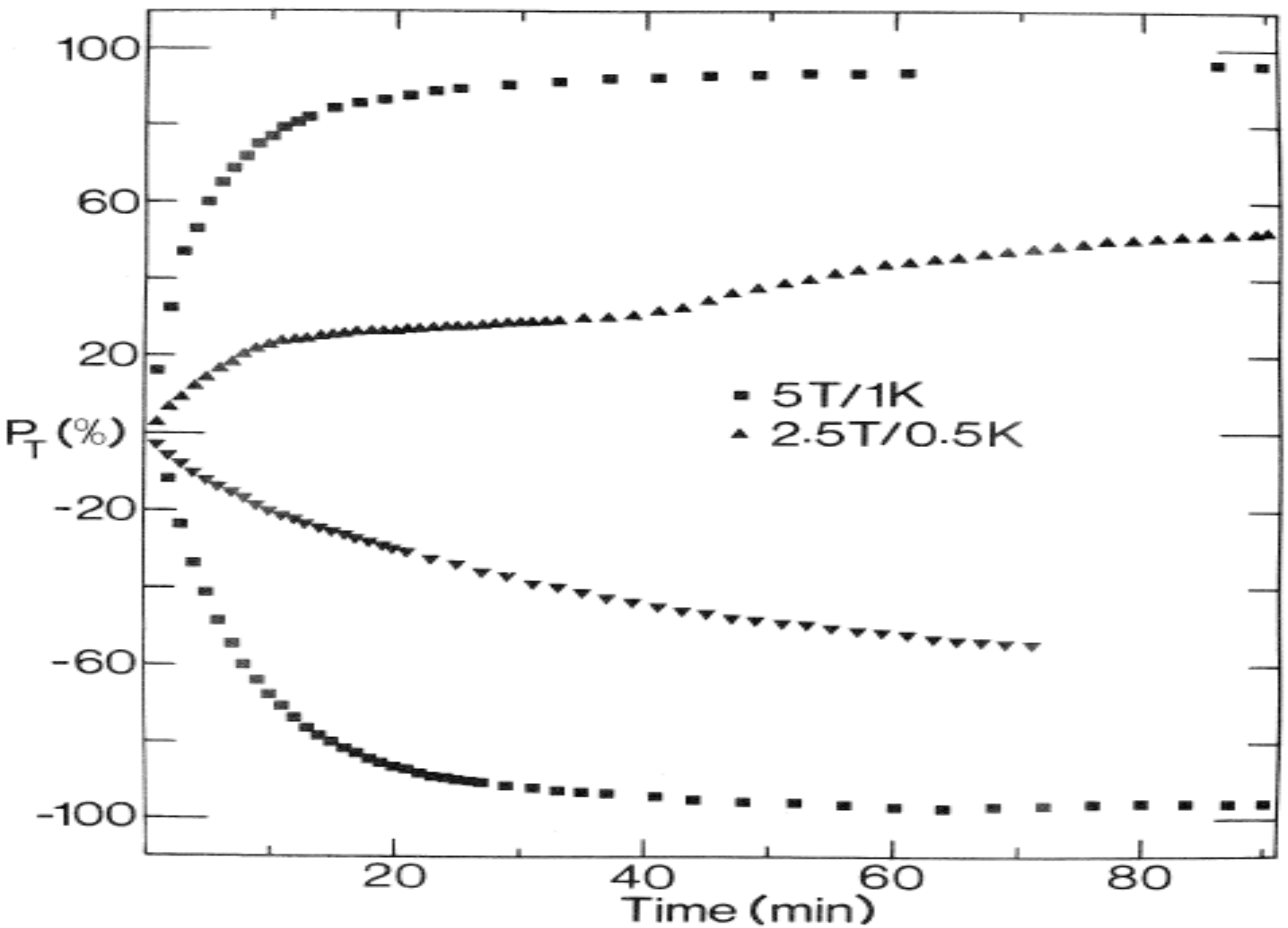
Era of Radiation Doping

- At the U. of Michigan and later at U. of Virginia started a program of irradiating Ammonia for experiments at Brookhaven, SLAC, Jlab.
- These experiments, using chemically doped butanol and diols
- suffered from radiation damage and a low proton content thus compromising the statistical precision of the experiment
- It was found by Crabb et al that at, 5T and 1K, that the proton polarization in $^{14}NH_3$ reached 90% in ~20 minutes, Reaching +95% and -98%. Approximately true for $^{15}NH_3$ as well
- Radiation damage was considerably better than other materials

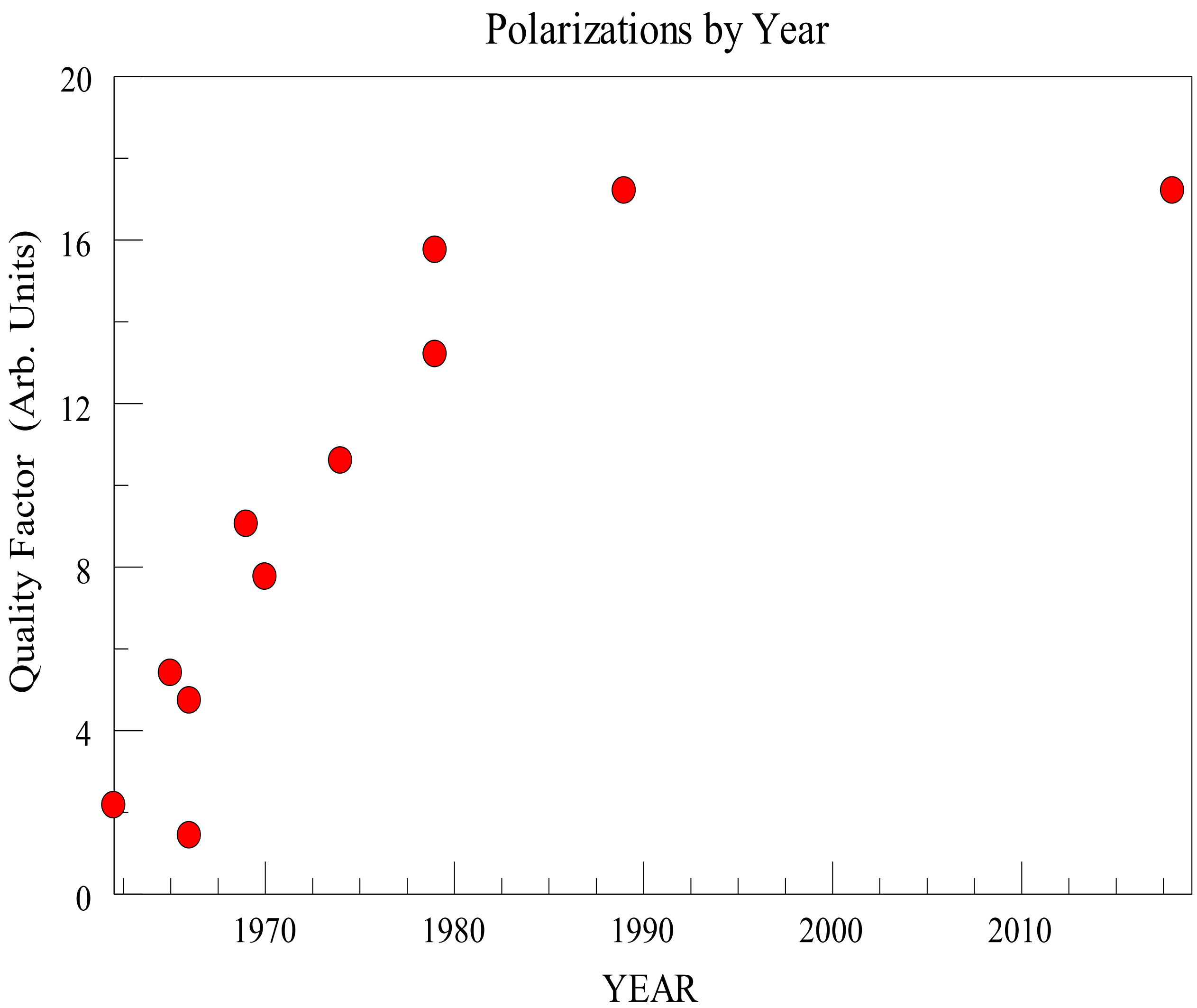
NH_3 and other Irradiated targets

- Ammonia used in many experiments CERN, SLAC, JLAB, Brookhaven, Bonn by many universities.
- Advantages: Higher dilution factor than butanol
- and diols 17.5% : ~10%
- Better rad. damage
- Problems Difficult handling, toxic

Ammonia Polarization



Material Quality by Year



Irradiation Follies

- Initially irradiations were done simply by irradiating an open dewar of liquid nitrogen by an electron beam, proton beam or gamma source.
- However:

Beam → LN_2 + O_3 → nitrates → move dewar -→ BOOM !!

Shift to more sophisticated cryogenic methods.

OR

Irradiate under liquid Argon

Problem: ^{40}A → ^{39}Cl $T_{1/2}$ ~ 55 mins proton knock-out at an electron energy of ~12 MeV

Run at 10 MeV with good extraction and ventilation

Deuterated Materials for Neutron Studies

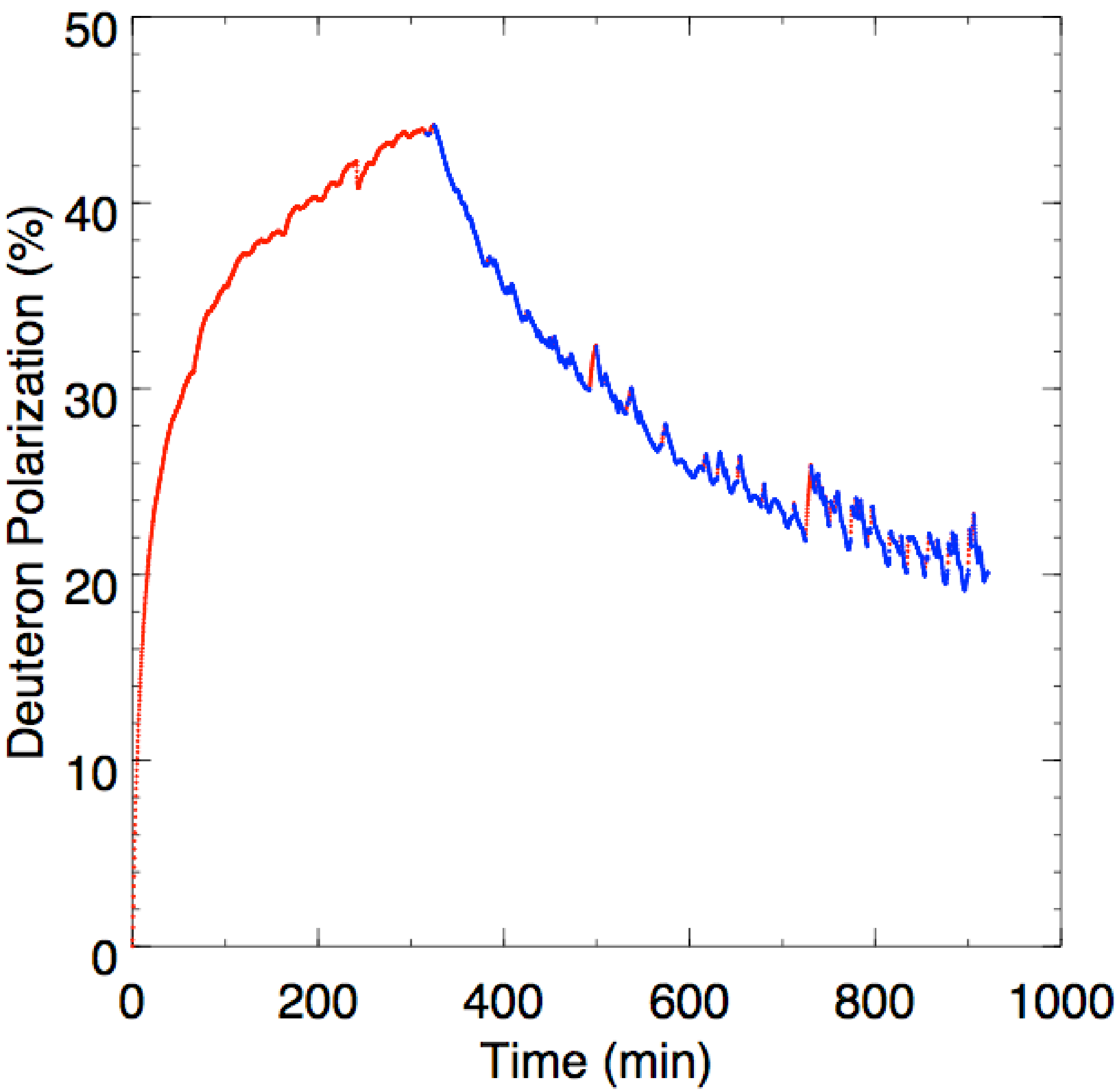
- Not aware of any LMN with D_2O
- Deuterated diols/butanol - deuteron polarizations ~30% to 50%
- However Meyer et al at Bochum using a trityl
- dopant in butanol achieved ~ 80% deuteron polarization with a dilution fridge and at 2.5 T.

Related to narrow ESR line for trityl

Irradiated deuterated materials

- ND_3
- Needs irradiation at 78K to reach polarizations of ~ 15 %, then subsequent *in situ* irradiation at ~1K to push to ~ 50%

ND_3 Polarization with SLAC Beam



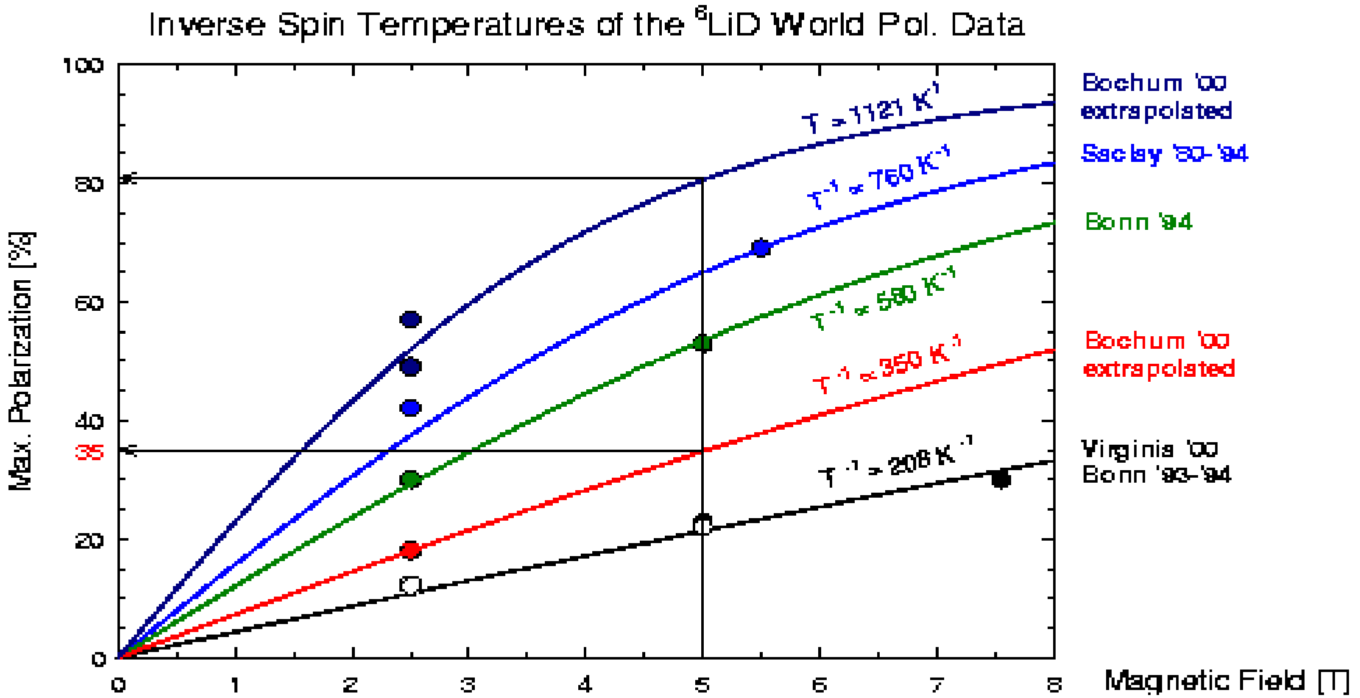
Lithium Deuteride

- ^{6}LiD
- Needs to be irradiated at 180 K. (Bochum). More complicated cryostat. → LN2 Cooled He gas.
- ^{6}Li can be considered as a combination of α + d leading to a dilution factor of ~ 50% (μ of Li ~ 3% less than of deuteron)

- First polarized at Saclay to 70% (6.5T, dil.fridge)
- Long polarizing times, less easy thermal calibrations.
- Better radiation damage characteristic than ammonia
- Used in two experiments at SLAC and then at CERN with COMPASS

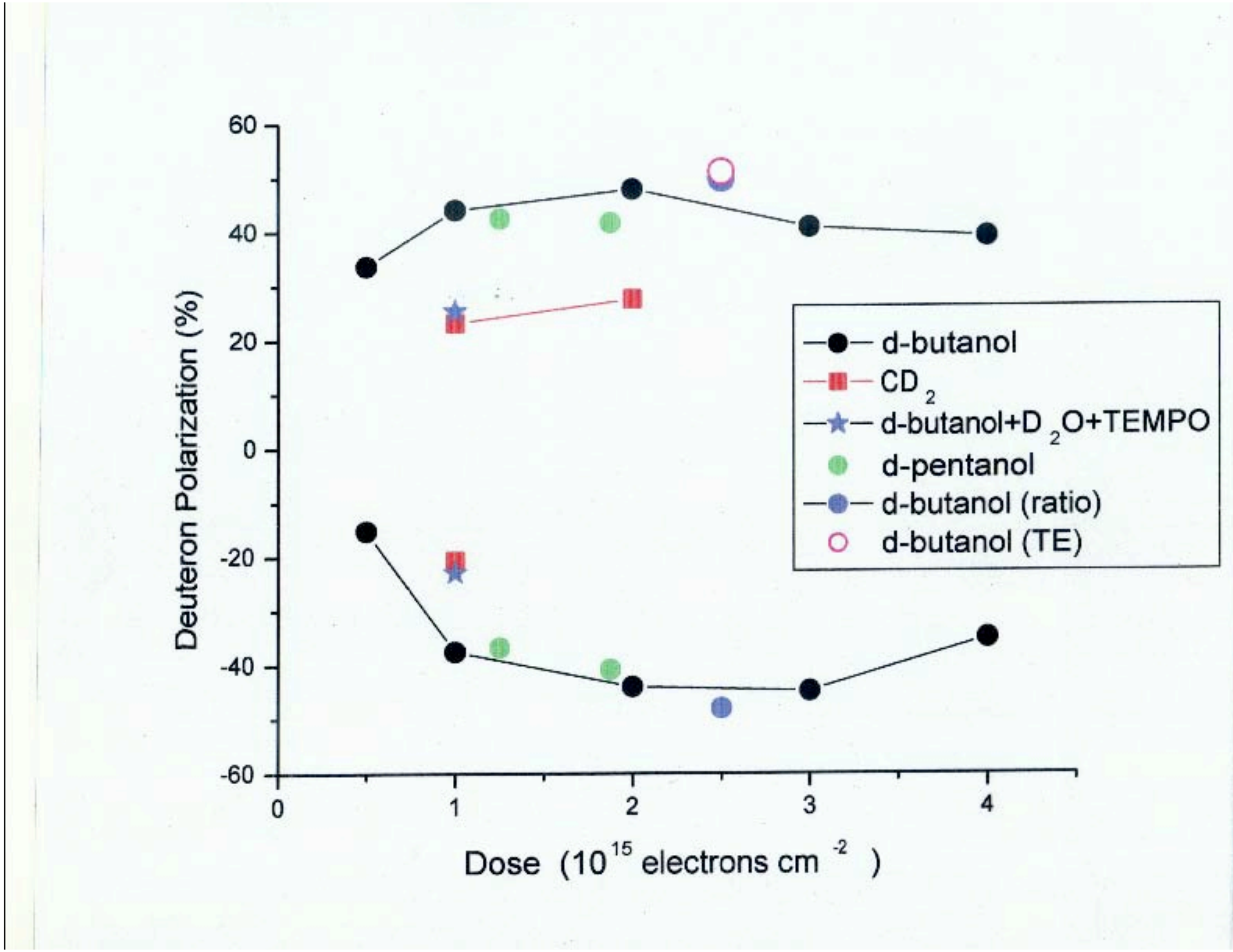
Deuteron Polarization in Lithium Deuteride

- ^{6}LiD



$$P = \frac{4 \tanh(g_d \mu_k B / 2kT)}{3 + \tanh^2(g_d \mu_k B / 2kT)} \sim 4/3\,(g_d \mu_k B / 2kT)$$

Deuteron polarizations vs dose for several materials



Deuteron polarization line shape at 63%

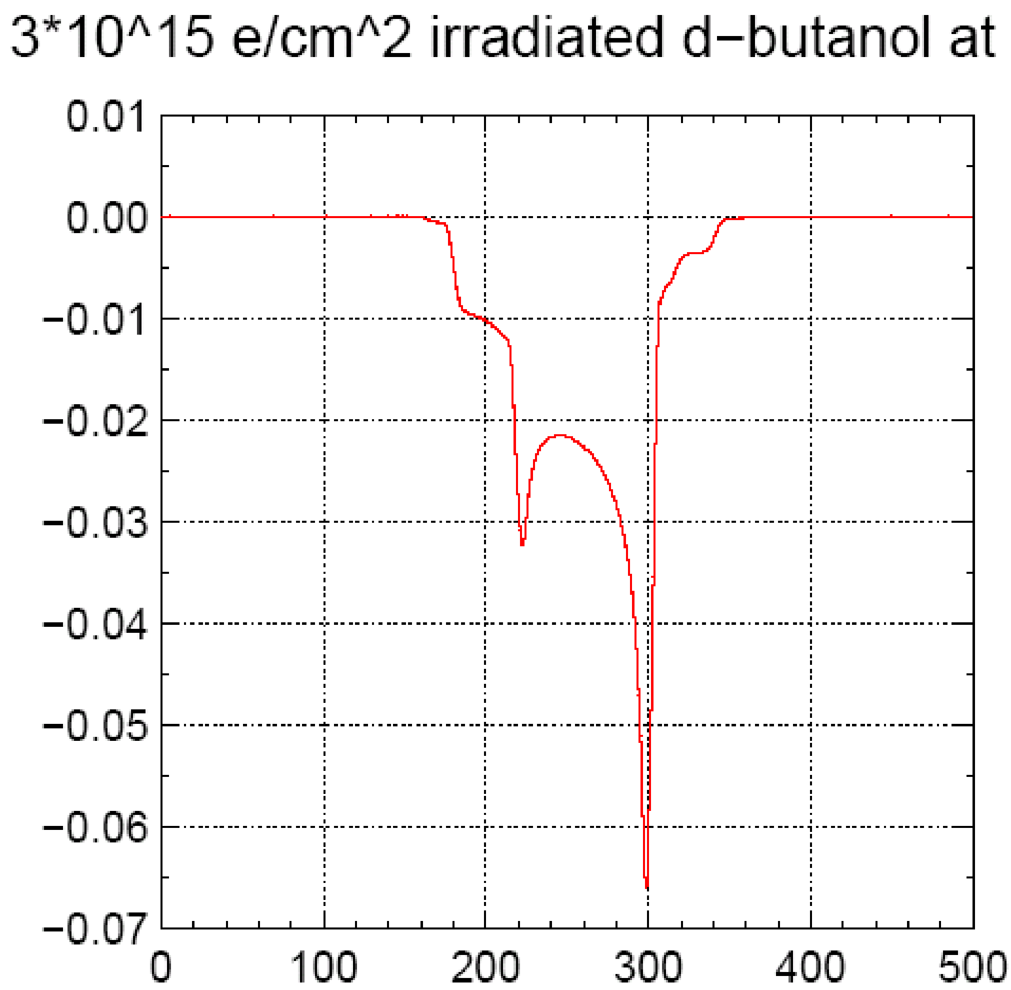


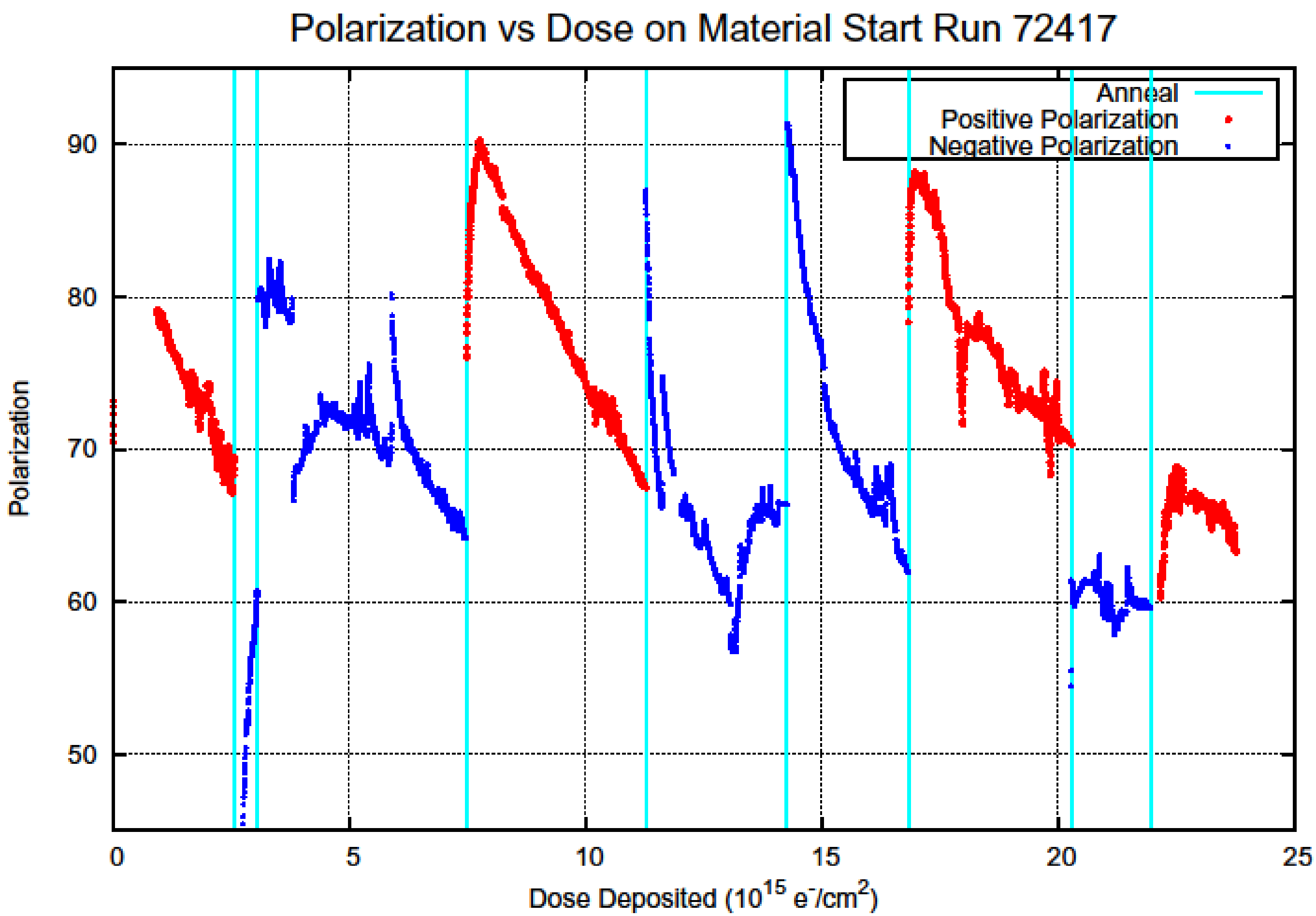
Table of Commonly used Polarized Target Materials

Table 1 Polarised target materials commonly used in particle scattering experiments

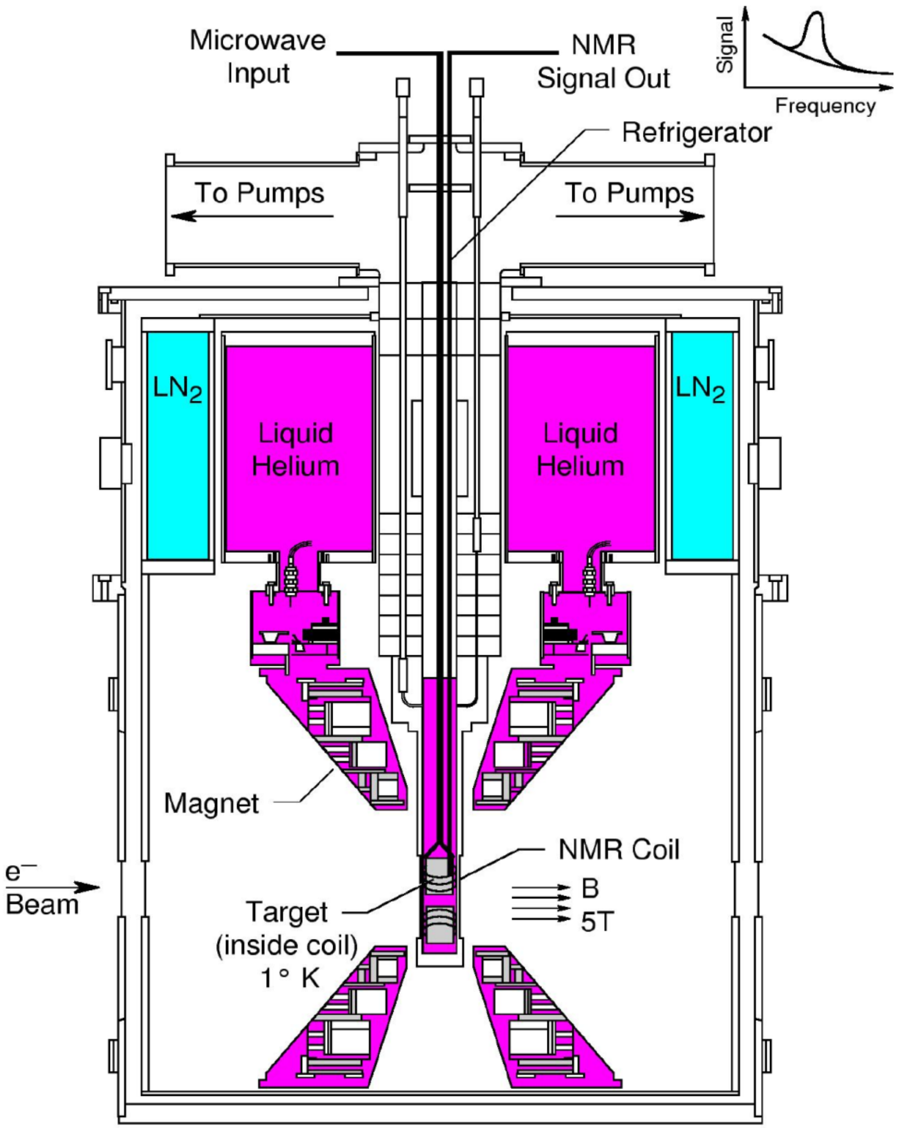
Materials & Chem. Comp.	Dopant[a] & Method	Polarizeable Nucleons % by weight	B/T Tesla/K	Max. Polarisation %	Radiation Damage Characteristic Flux[b] 10^{14} particles/cm^2
LMN $La_2(Co, Mg)_3(NO)_3 \cdot 24H_2O$	Neodymium Ch	3.1	2.0/1.5	±70	~ 0.01
1,2 Propanediol $C_3H_6(OH)_2$	Cr (V) Ch	10.8	2.5/0.37	+98 –100	~ 1
1,2 Ethanediol $C_2H_4(OH)_2$	Cr (V) Ch	9.7	2.5/0.5	±80	~ 2
Butanol C_4H_9OH	EHBA Cr (V) Ch	13.5	2.5/0.3	±93	3 - 4
EABA $C_2NH_7BH_3NH_3$	EHBA Cr (V) Ch	16.5	2.5/0.5	+75 –73	7(+), 3.5(–)[c]
Ammonia $^{14}NH_3$, $^{15}NH_3$	$NH_2\bullet$ Ir	17.6, 16.6	5.0/1.0	+97 –100	7, 17.5[d]
d-Butanol C_4D_9OD	EDBA Cr (V) Ch	23.8	2.5/0.3	±80	not measured
d-Ammonia $^{14}ND_3$, $^{15}ND_3$	$ND_2\bullet$ Ir	30.0, 28.6	3.5/0.3	+49 –53	13(+), 28(–)
Lithium deuteride ^6LiD	f-center Ir	50	6.5/0.2	±70	> 100

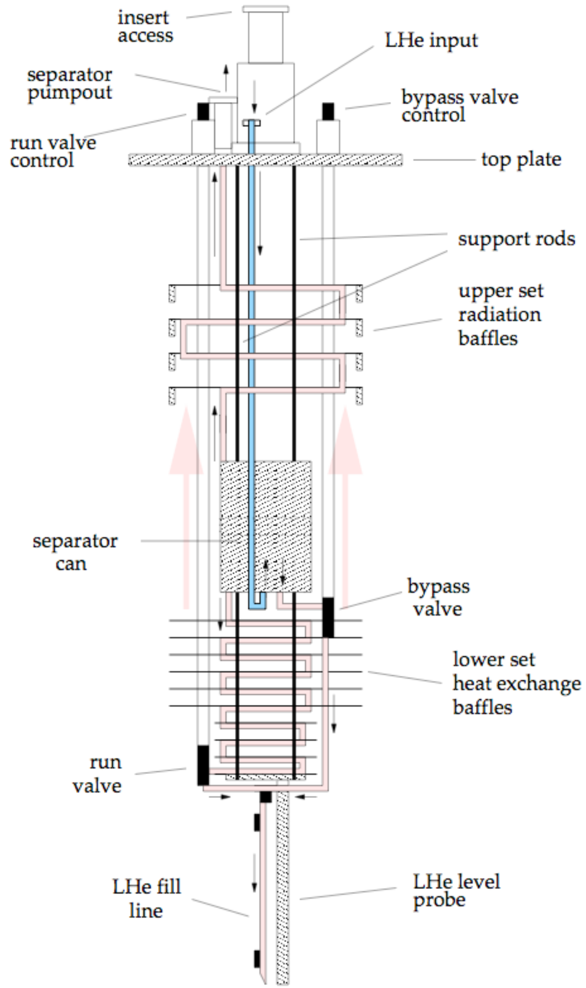
[a] Ch: chemically doped, Ir: doped through irradiation
[b] The radiation dose which reduces the polarization by e^{-1} of its value
[c] For positive and negative polarizations, respectively
[d] In NH_3 there are two distinct regions of decay

Radiation Damage in Ammonia vs Dose



UVA Polarized Target

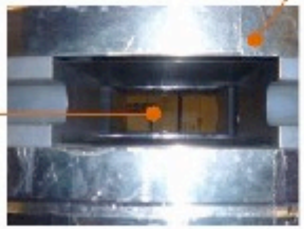




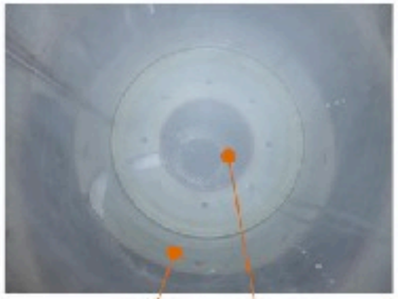
Putting it all Together

Final preparations and run

put vacuum chamber back together



leak checked fridge shell + nose



Cryogenic Performance

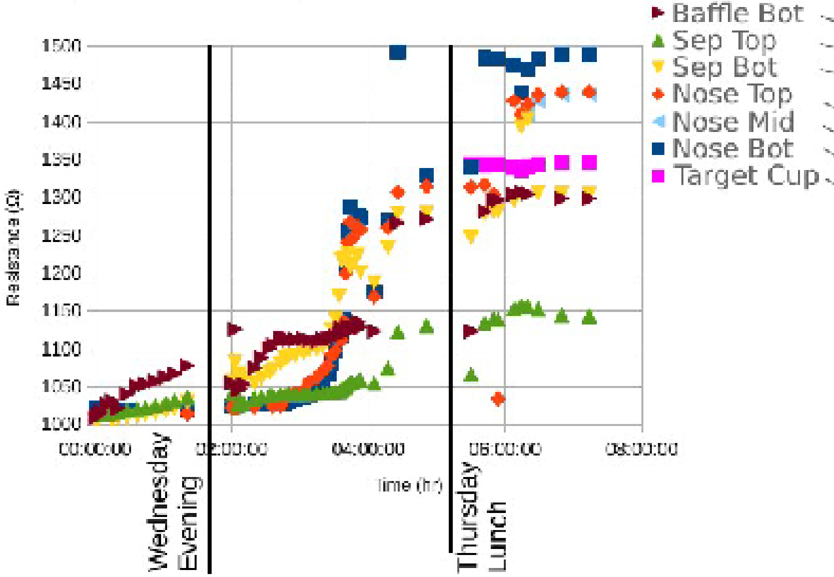
Test results

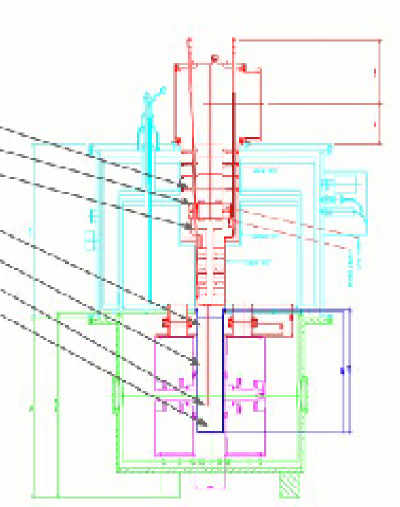
Fridge performance

separator and nose fill

~1hr to fill the nose after a night on standby

very stable, very little attention required





POLARIZED TARGET SUBSYSTEMS

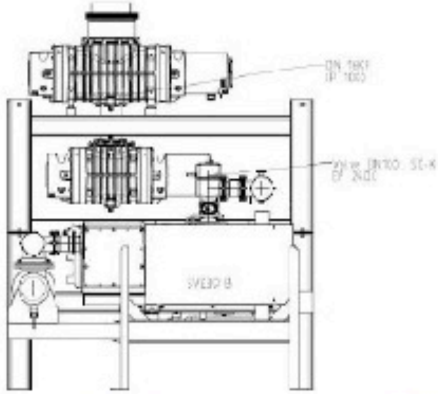
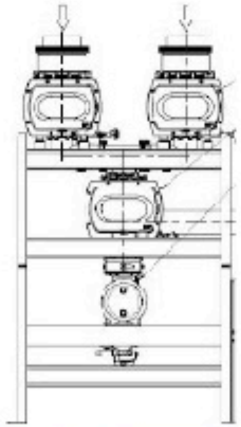
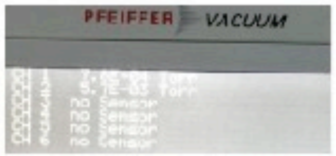
Magnet — Fridge — Insert — NMR — Microwave — **Pumps** — Target material

Pumping system

- designed and built by Oerlikon
- target heat load ~1.4W
- μ-wave:~1W, beam:~0.37W
- 3 roots (7000), 1 rotary vane (840)
- requires 100L LHe per day
- 14000 m3/hr pumping capacity

Construction and tests

- first assembly at LANL spring 2015
- tested and shipped to FNAL
- assembled and tested 10/2015

Recent Projects and Achievements

Fast target helicity flips through Adiabatic Fast Passage (AFP)

AFP at UVA

performed AFP on different materials (5T, 1K)

15NH3, D-butanol, butanol+tempo

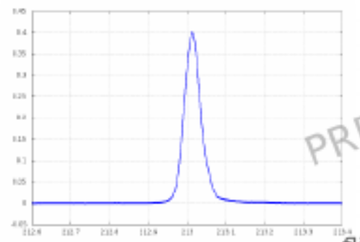
preliminary results on flip efficiency

Table 1
Results from AFP experiments with various nuclei in differ target materials

Nuclei	Substance dopant	e^- conc. (spins/g)	δP
^{1}H	1-butanol EHBA-Cr(V)	2.0×10^{19}	-0.76
^{7}Li / ^{1}H	^{7}LiH (irradiated)	low	≈0.90 / -0.90
^{19}F / ^{1}H	8-fluoro-1-pentanol TEMPO	1×10^{20}	-0.37 / -0.40
^{2}H	1-butanol-d_{10} / EHBA-Cr(V)-d_{22}	2.36×10^{19} / 6.35×10^{19}	-0.92 / -0.90

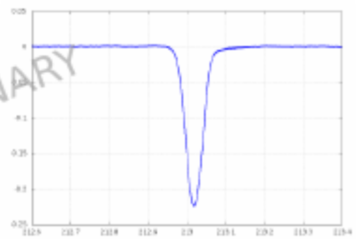
NIM 356 (1995) 108

15NH3



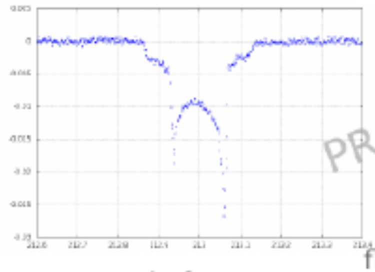
before

flip efficiency 0.55



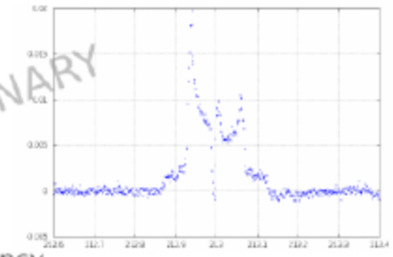
after

D-Butanol

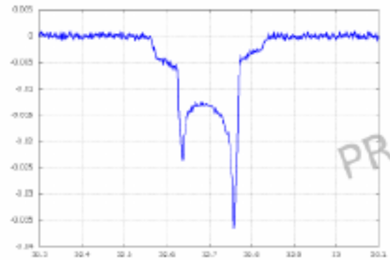


before

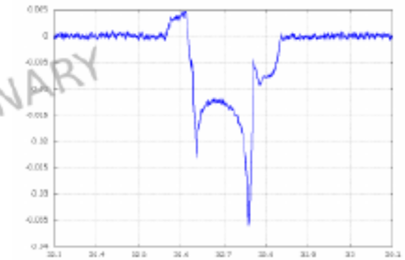
flip efficiency >0.8



after



before



after

AFP produces rotation of the macroscopic magnetization vector by sweeping through resonance in a short time compared to the relaxation time

- Set record for Tensor Polarization for Deuteron (d-b only) Q>31% @1K 5T
- Set record for AFP flip with Proton e>50% @ 1K 5T

New Use of AFP

Fast target helicity flips through Adiabatic Fast Passage (AFP)

AFP at UVA

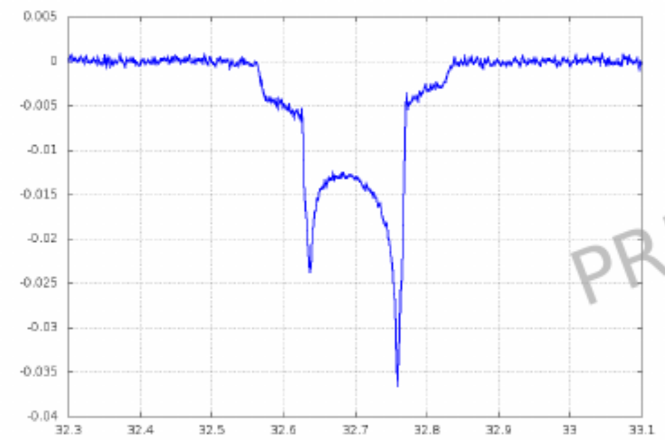
- performed AFP on different materials (5T, 1K)
- 15NH3, D-butanol, butanol+tempo
- preliminary results on flip efficiency

Table 1
Results from AFP experiments with various nuclei in different target materials

Nuclei	Substance dopant	e^- conc. (spins/g)	δP^{max}
^1H	1-butanol EHBA-Cr(V)	2.0×10^{19}	-0.76
^7Li ^1H	^7LiH (irradiated)	low	-0.90 -0.90
^{19}F ^1H	8-fluoro-1-pentanol TEMPO	1×10^{20}	-0.37 -0.40
^2H	1-butanol-d_{10} EHBA-Cr(V)-d_{22}	2.36×10^{19} 6.35×10^{19}	-0.92 -0.90

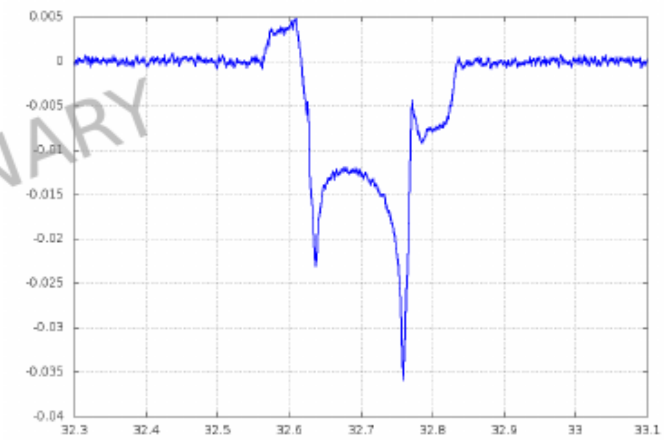
NIM 356 (1995) 108

D-Butanol pedestal flip

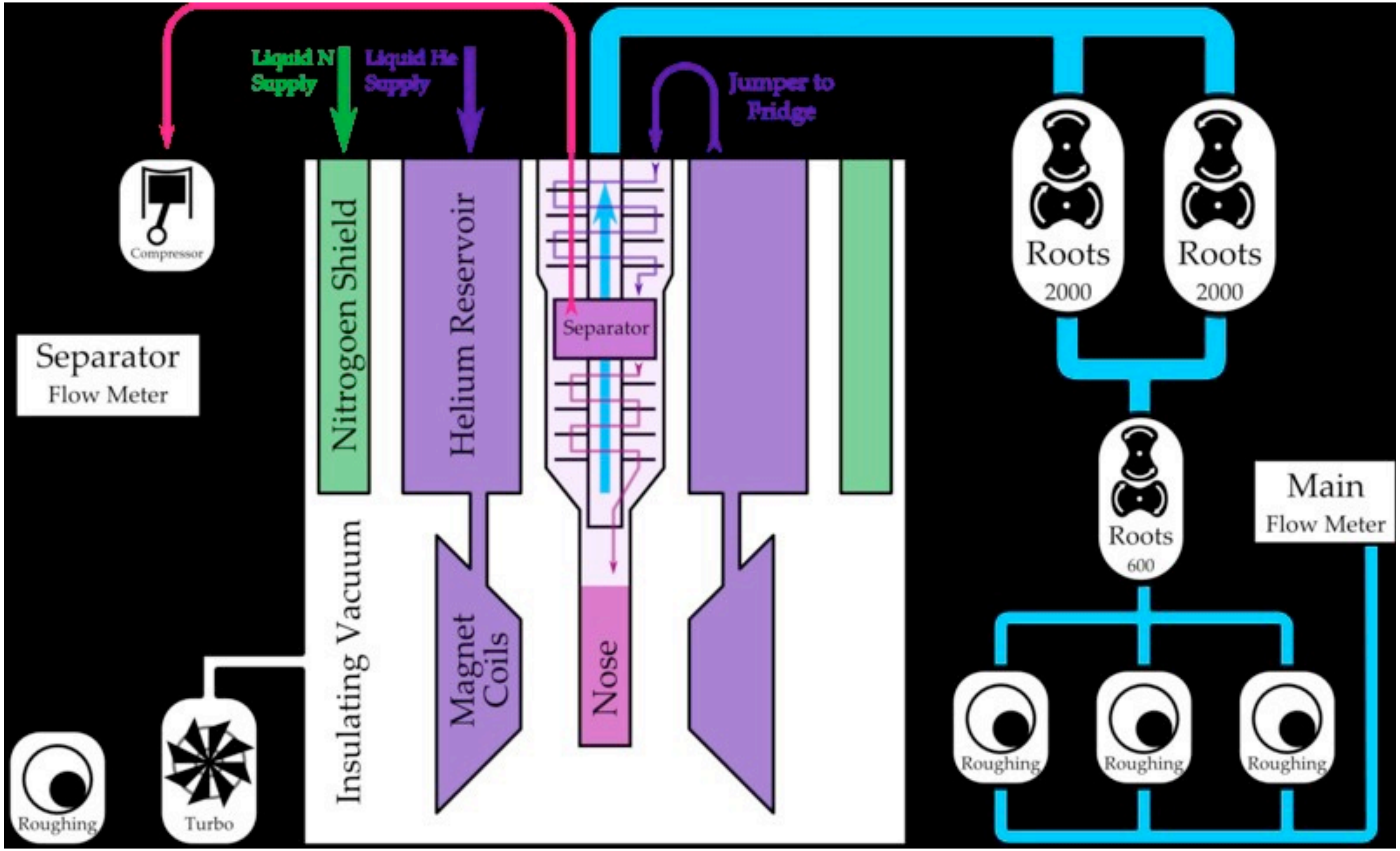


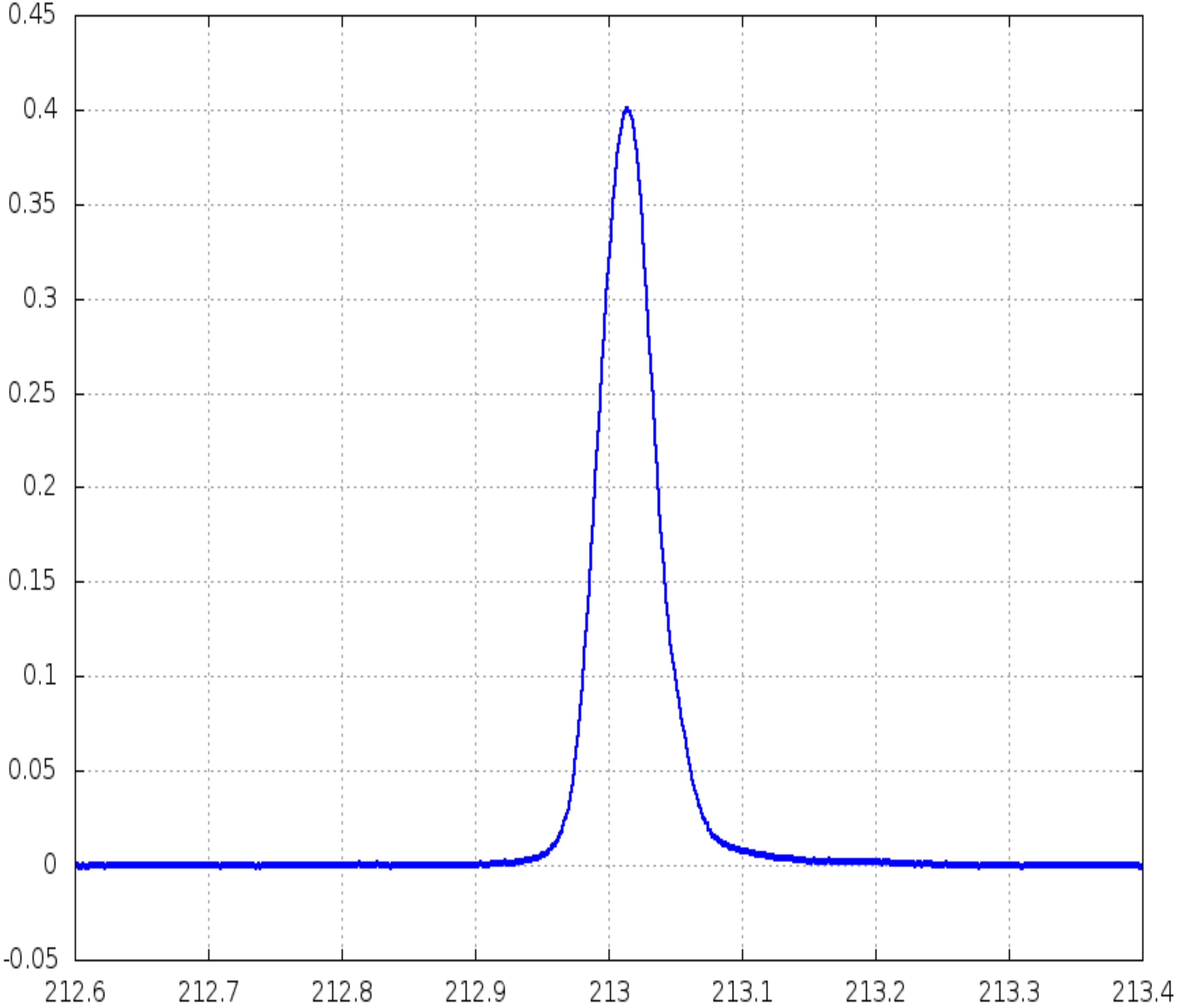
before

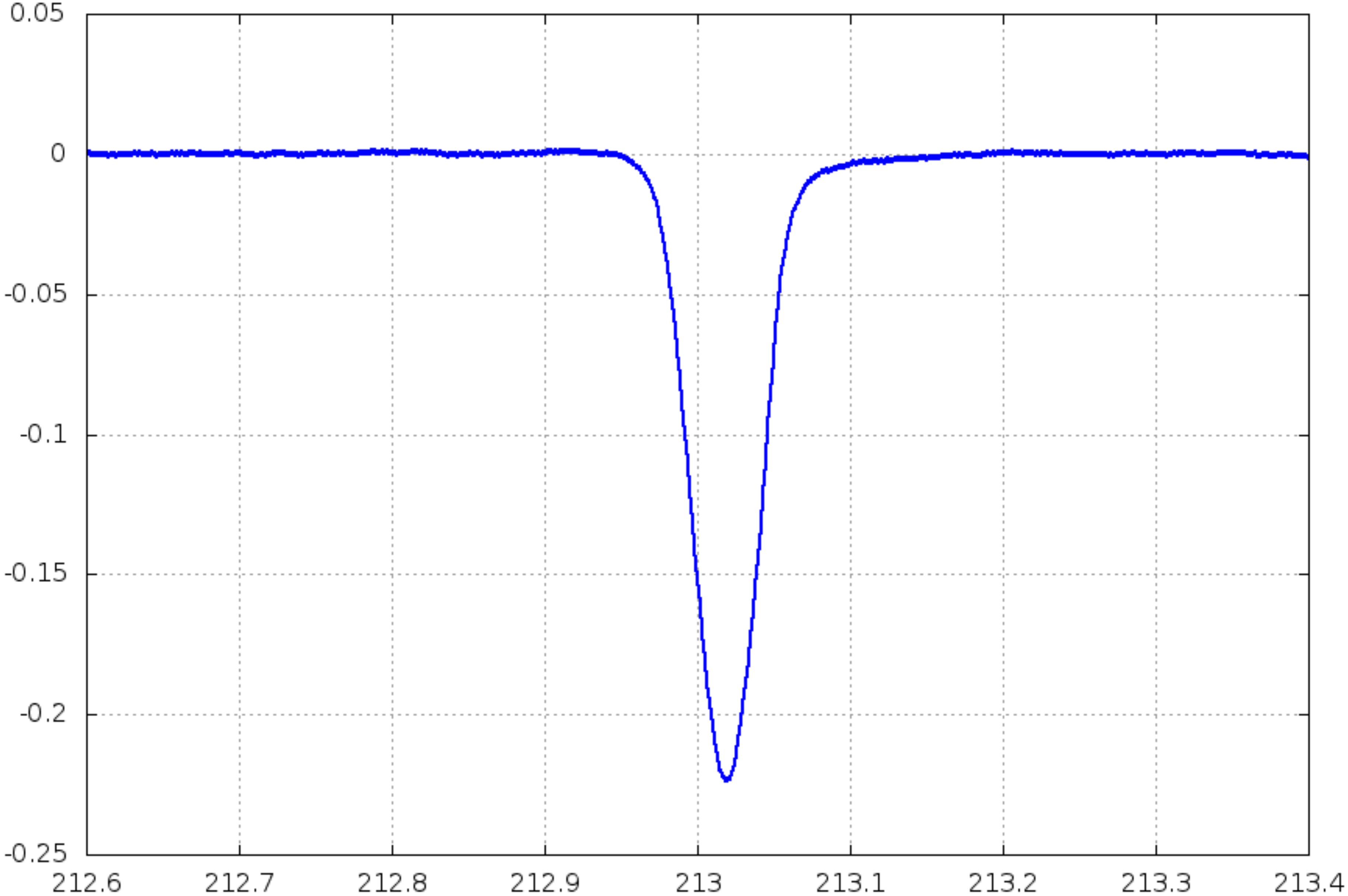
PRELIMINARY



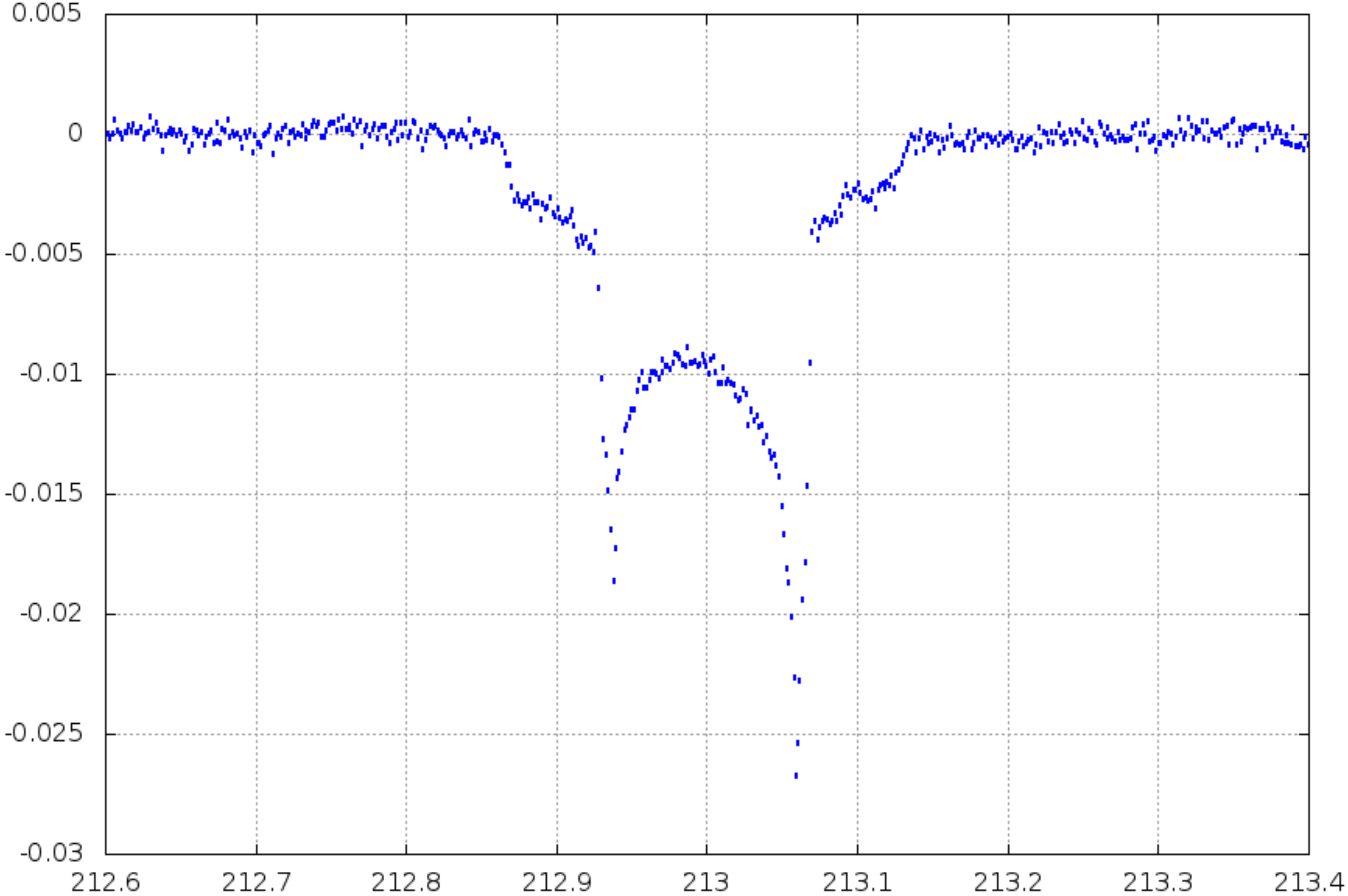
after

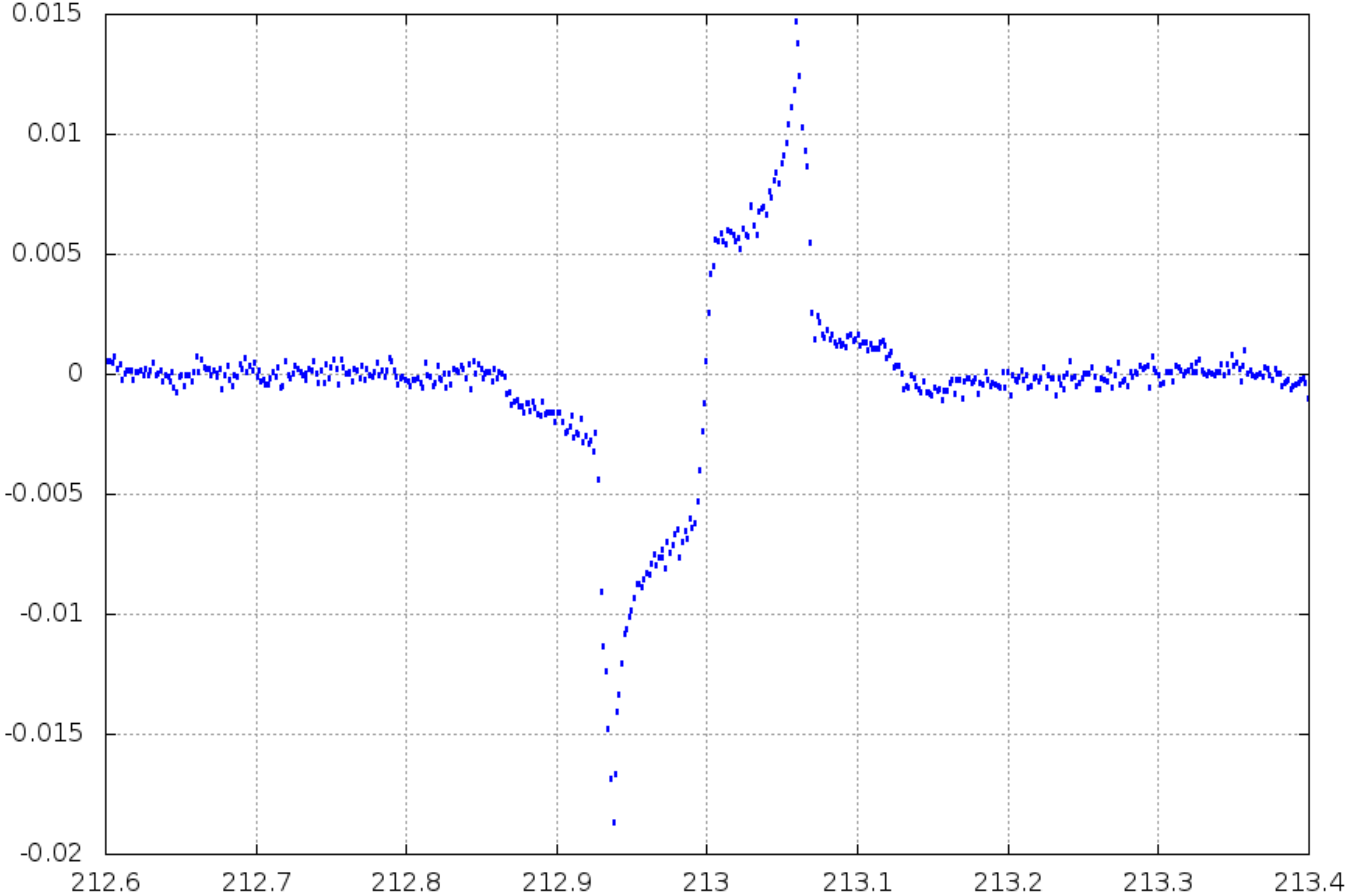

Liquid N
Supply
Liquid He
Supply
Jumper to
Fridge
Compressor
Separator
Flow Meter
Nitrogoen Shield
Helium Reservoir
Separator
Insulating Vacuum
Magnet
Coils
Nose
Roots
2000
Roots
2000
Roots
600
Main
Flow Meter
Roughing
Turbo
Roughing
Roughing
Roughing

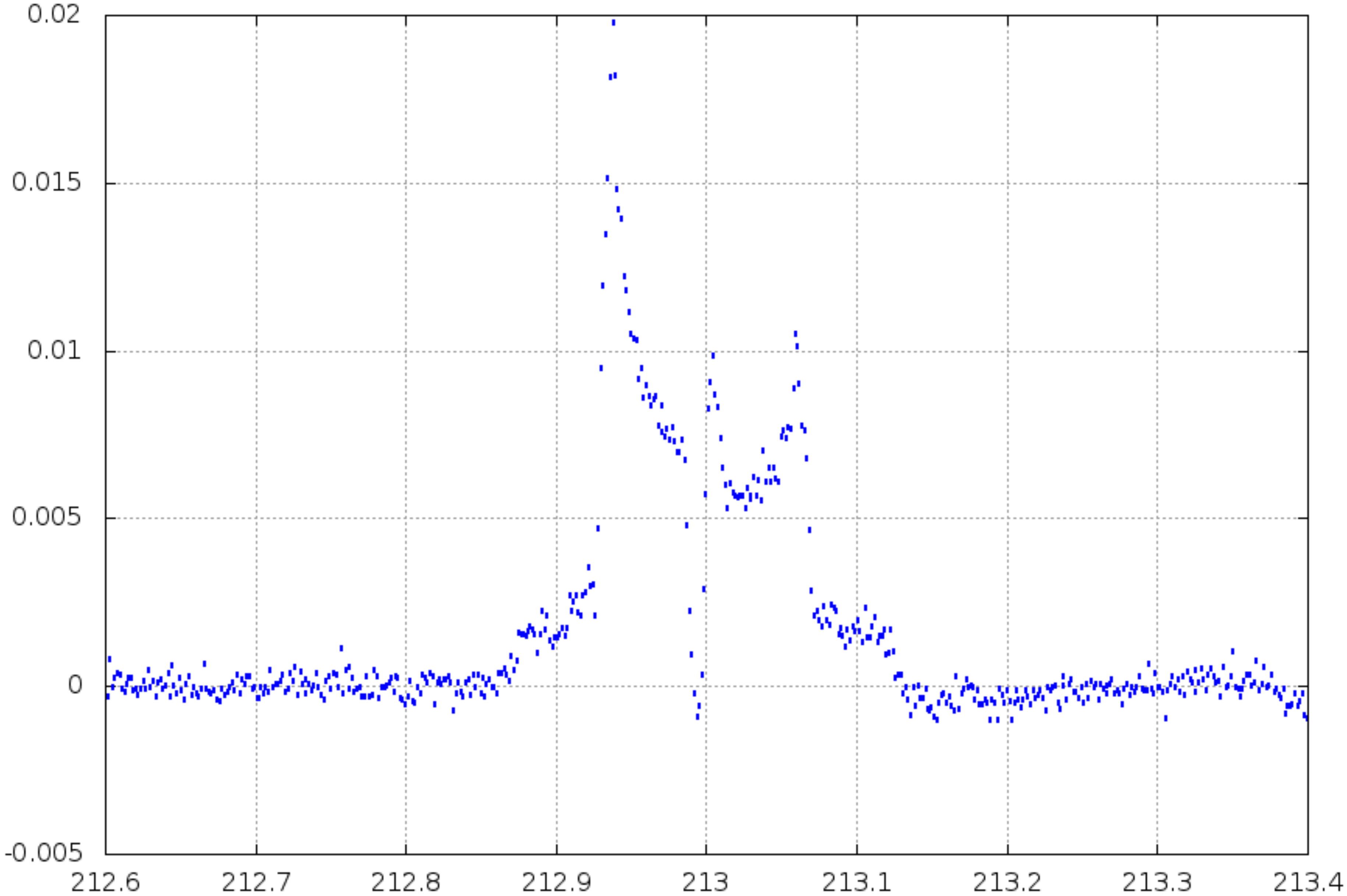

0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
-0.05
212.6
212.7
212.8
212.9
213
213.1
213.2
213.3
213.4



0.05
0
-0.05
-0.1
-0.15
-0.2
-0.25
212.6
212.7
212.8
212.9
213
213.1
213.2
213.3
213.4


0.005
0
-0.005
-0.01
-0.015
-0.02
-0.025
-0.03
212.6
212.7
212.8
212.9
213
213.1
213.2
213.3
213.4


0.015
0.01
0.005
0
-0.005
-0.01
-0.015
-0.02
212.6
212.7
212.8
212.9
213
213.1
213.2
213.3
213.4


0.02
0.015
0.01
0.005
0
-0.005
212.6
212.7
212.8
212.9
213
213.1
213.2
213.3
213.4