

# Adiabatic Demagnetization Refrigeration

External magnetic field (B) aligns ...
 Thermal disorder (T) mixes up ...

degree of order (M) depends on the ratio B/T



Measure M in known B and get TOR Fix  $M \Longrightarrow$  change in Bresults in change in T

Thermodynamics of Zeeman system:  $x = \frac{\mu B}{k T}$ Partition function  $Z = \left[\sum_{n=1}^{+J} e^{-m x/J}\right]^{nN_A} = \left[\sinh \frac{(2J+1)x}{2J} / \sinh \frac{x}{2J}\right]^{nN_A}$ m = -Jgives - Entropy S:  $\frac{S}{nR} = \frac{\partial (T \ln Z)}{\partial T}$  $=\frac{x}{2 I} \operatorname{coth} \frac{x}{2 I} - \frac{(2 J+1) x}{2 I} \operatorname{coth} \frac{(2 J+1) x}{2 I} + \ln \left[ \sinh \frac{(2 J+1) x}{2 I} \sinh^{-1} \frac{x}{2 I} \right]$ – Heat capacity C:  $\frac{C_B}{nR} = T\left(\frac{\partial (S/nR)}{\partial T}\right)_{p} = \frac{x^2}{4 I^2} \sinh^{-2} \frac{x}{2 I} - \frac{(2J+1)^2 x^2}{4 I^2} \sinh^{-2} \frac{(2J+1)x}{2 I}$ - Magnetization M:  $\frac{M}{N\mu} = \frac{M}{M\mu} = \frac{k_B T}{N\mu} (\frac{\partial \ln Z}{\partial B})_T = B_J(x)$  $= \frac{2J+1}{2L} \operatorname{coth} \frac{(2J+1)x}{2L} - \frac{1}{2L} \operatorname{coth} \frac{x}{2L}$ 

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2

#### High-*T* approximations

Often  $x \ll 1$   $(k_B T \gg \mu B)$  so that it is safe to simplify

$$\frac{S}{nR} \approx \ln(2J+1) - \frac{J+1}{6J}x^2$$
$$\frac{C_B}{nR} \approx \frac{J+1}{3J}x^2$$
$$\frac{M}{M_{sat}} \approx \frac{J+1}{3J}x$$

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3

Entropy

All relations above, including molar spin entropy  $S_n = S/n$ , depend just on the ratio of magnetic field and temperature:

 $S_n = S_n \left( B/T \right)$ 

The limiting value at high temperatures:

$$S_n \xrightarrow[T \to \infty]{} S_{n, \max} = R \ln(2J+1)$$

In adiabatic processes entropy remains constant  $\Rightarrow T$  can be made to change in proportion to *B*. BUT entropy must differ notably from its maximum value to begin with.

#### Internal magnetic field

The spins do not respond to external magnetic field only, they also feel the weak fields of each other. This is represented by the internal field b.



Roughly speaking  $b \sim k_B T_c / \mu$ , where  $T_c$  is the magnetic ordering temperature of the material

This adds quadratically to the external magnetic field:

$$B_{tot} \approx \sqrt{B^2 + b^2}$$

To have  $B_{tot} \sim B$ , one must have rather small b=> we are interested on materials with low  $T_c$ , i.e. weakly magnetic materials

# Magnetic refrigeration

- Initial condition with low entropy  $S = S_i < S_{max}$  ( $\Delta S/S_{max} > 0.1$ ) has to be prepared by high field  $B_i$  / low temperature  $T_i$
- No other entropy in the system should be comparable to this
- The system must be made isolated (adiabatic); heat switch needed
- The magnetic field must be changed reversibly => corresponding change in temperature (B/T = const.)
- The weaker the magnetic system, the larger  $B_i/T_i$  is needed BUT the lower final temperature is achievable, as  $B_{min} \sim b$
- Cooling capacity depends on final field & moment strength
- When the cooling capacity is exhausted, the process has to be repeated again (single cycle cooling)

# Cooling cycle



- Precool to point A:  $B_{ext} = 0$ ,  $T = T_i$
- Magnetize  $A \rightarrow B$ , remove heat  $Q_{AB} = T \varDelta S$
- Isolate the system,  $\Delta S = 0$  thereafter
- Demagnetize  $B \rightarrow C$

 $Q_{\rm CA} \ll Q_{\rm AB}$ 

• Use the capacity  $C \to A$ ,  $Q_{CA} = \int_{T_f}^{T} T \left(\frac{\partial S}{\partial T}\right)_B dT = \int_{T_f}^{T} C_B dT$ 

Fig. 9.1. Molar entropy of a single crystal of the paramagnetic salt CMN with angular momentum J = 1/2 (Sect. 9.4) as a function of temperature for magnetic fields applied along the cystallographic a axis. For the refrigeration process the salt is first isothermally magnetized (AB), and then after thermal isolation adiabatically demagnetized (BC). Eventually it warms up along the entropy curve at the final demagnetization field, which is zero in the example shown. The heat of magnetization during magnetization is given by the rectangle  $ABDS_{\infty}$ . The cooling power of the salt after demagnetization is given by the shaded area [9.4]



# Conventional magnetic refrigeration

- Uses dilute paramagnetic salts (CMN, CPA, FAA, ...)
- Easy initial conditions  $B_i = 1$  T and  $T_i = 1$  K are sufficient
- High cooling capacity remains also at  $B_{ext} = 0$
- Temperature can be measured from inherent property:  $\chi = \lambda/T$
- Fast, demagnetization can be performed in few minutes

BUT

- Poor thermal conductivity limits heat transfer
- Difficult to mount samples (except liquid <sup>3</sup>He immersed in powdered CMN salt; 2 mK can be achieved)
- Single shot cooling

Largely replaced by dilution refrigerators Space applications are still developed

# Realizations



### Adiabatic nuclear demagnetization

Many isotopes carry a nonzero nuclear spin
Very small moment, of order nuclear magneton

$$\mu_{n} = \frac{e\hbar}{2m_{n}} = \frac{m_{e}}{m_{n}} \mu_{B} \approx \mu_{B} / 1840 \approx 5.05 \cdot 10^{-27} \text{ J/T}$$
$$= T_{c} \sim \text{pK} \dots \mu \text{K}$$

- Very low temperatures can be achieved
- Moments need not be diluted
   => good moment density (more heat capacity)
- Metals can (must) be used
  - Good thermal conductivity
  - Reasonable thermal contacts

#### The challenge

Small  $\mu \implies$  need very large  $B_i/T_i$ 

For example:  $\begin{cases} T_i = 10 \text{ mK} \\ B_i = 6 \text{ T} \end{cases}$ 

$$\Rightarrow \Delta S/S_{max} = 5\%$$
 for Cu



To maintain sufficient heat capacity, one cannot demag. to zero field (for nuclear magnets  $b \sim 0.1 \text{ mT}$ )

Usually  $B_f \sim 10 \dots 100 \text{ mT}$  (limits achievable  $T_f$ )

#### Possible material choices

- Pure metal for sufficient thermal conductivity
- Reasonable moment, high isotope abundance
- No strong superconductivity or electronic magnetism
- Spin lattice coupling has to be sufficient
- Large spin may or may not be good

Candidates with  $\sim 100\%$  abundance:

isotope	$\mu/\mu_n$	Ι	note
<sup>27</sup> Al	3.64	5/2	SC, $B_c = 10$ mT, tolerable
<sup>03,03</sup> Cu 113,115In	2.3	$\frac{3}{2}$	SC = R = 30  mT questionable
$^{51}V$	5.14	9/2 7/2	SC, $B_c = 50$ mT, questionable SC, $B_c = 0.1$ T, ruled out
<sup>93</sup> Nb	8.07	9/2	SC, $B_c = 0.2$ T, ruled out

#### Further requirement

• Cubic lattice or spin I = 1/2

otherwise electric field gradient at nuclear positions may produce large quadrupole splitting (unless I = 1/2), which contributes to b, possibly making it too large

For example, indium has tetragonal lattice, whereby the quadrupole moment produces an effective field

 $b_q \sim 0.25 \text{ T} \implies$  demagnetization is limited to this

All in all, <u>copper</u> is the best choice (aluminum might do in some cases)

#### Thermodynamics (again)

• High temperature expansions are sufficient in most cases

$$\frac{S}{nR} \approx \ln(2J+1) - \frac{J+1}{6J}x^2$$
$$\frac{C_B}{nR} \approx \frac{J+1}{3J}x^2$$
$$\frac{M}{M_{sat}} \approx \frac{J+1}{3J}x$$



Fig. 10.4. Nuclear heat capacities as a function of temperature for Al (I = 5/2), Cu (I = 3/2), Tl, Pt and Ag (I = 1/2) (however, remember that Pt contains only 33.8% of <sup>195</sup>Pt, its only isotope with a nuclear moment). The lower temperature scale corresponds to heat capacity data in a magnetic field of 9 T, the upper temperature scale to data in a field of 7 mT

#### Cooling cycle

- 1) Magnetize to  $B_i$  (1 ... 2 h), usually as quickly as the magnet permits (large heat of magnetization, DR copes with it better,  $T_1 \sim 50$  ... 100 mK)
- 2) Precool to  $T_i$  (one to several days) nuclear stage (NS) size + efficiency of DR + quality of heat switch
- 3) Thermal isolation of the nuclear cooling stage (15 min) superconducting heat switch between the DR & NS made SC
- 4) Demagnetization to  $B_f \sim 10 \dots 100 \text{ mT} (1/2 \dots 1 \text{ day})$ speed limit is set by losses due to eddy current heating
- 5) Thermalize the experiment (hours ... days)
- 6) Maintain the low T (days ... weeks)
- Connect NS to DR (heat switch made normal by magnetic field) for the next precool; GOTO 1)

#### Precooling

Dilution refrigerator absorbs heat  $\dot{Q} = a T_{DR}^2 - \dot{q}$ ;  $a = 84 \dot{n} \text{ J/(mol K}^2)$ 

where  $\dot{q}$  is the background heat load

Base temperature without extra load is  $T_0 = \sqrt{\dot{q}/a}$ 

Thermal resistance of the link between NS and DR (heat switch in normal state) is characterized by the coefficient  $R \sim 2 \dots 20$  K<sup>2</sup>/W, giving

$$2R\dot{Q} = T_{NS}^2 - T_{DR}^2$$

The power  $\hat{Q}$  originates from heat of magnetization of nuclear spins

$$dQ = -C_B dT_{NS} ; C_B = \frac{V\lambda}{\mu_0} \frac{B^2}{T_{NS}^2}$$

Precooling time to temperature *T* can be solved from these:

$$t(T) = \left(\frac{1}{a} + 2R\right) \frac{V\lambda B^2}{\mu_0 T_0^2} \left(\frac{1}{2T_0} \ln \frac{T + T_0}{T - T_0} - \frac{1}{T}\right) \approx \left(\frac{1}{a} + 2R\right) \frac{V\lambda B^2}{3\mu_0 T^3}$$

### Demagnetization

Change of magnetic field must be made as reversibly as possible Losses may be assumed to result from

- $\text{ constant background heat load } \dot{q}_{NS} \\ \text{ induced eddy current heating } \gamma \dot{B}^2 \Big\} \quad \dot{Q}_{NS} = \dot{q}_{NS} + \gamma \dot{B}^2$

where  $\gamma = \Gamma V RRR/\rho_0$  depends on el. resistivity and geometry

for a cylinder  $\Gamma = r^2/8$ 

for a slab  $\Gamma = d^{2}/12$ 





### Eddy currents

To reduce detrimental influence of eddy currents, the nuclear stage must be constructed from thin filaments or slabs

2r or  $d \sim 1$  mm or less



Filling factor should be good, but the slabs or filaments must be insulated from each other (from the flat side)

# Optimum demagnetization

Best possible demagnetization in time  $t_{dm}$  has parabolic profile:

$$B(t) = a (t/t_{dm})^{2} - b (t/t_{dm}) + B_{i} \begin{cases} a = B_{i} + B_{f} - \sqrt{4} B_{i} B_{f} + (\dot{q}_{NS}/\gamma) t_{dm}^{2} \\ b = 2 B_{i} - \sqrt{4} B_{i} B_{f} + (\dot{q}_{NS}/\gamma) t_{dm}^{2} \end{cases}$$
  
For example:  $n_{Cu} = 100 \text{ mol} \\ d = 2 \text{ mm}, w >> d \\ RRR \sim 1000 \end{cases} \implies \gamma = 10.6 \text{ Ws}^{2}/\text{T}^{2}$ 

$\dot{q}_{\rm NS} = 10 \text{ nW}$	demag. time	profile	$\log \Delta(B_f/T_f)/(B_i/T_i)$
$B_i = 9T$	$t_{opt} = 3$ days	linear	1.2 % (too slow)
$T_i = 10 \text{ mK}$	10 h	linear	5 % (reasonable)
$B_f = 50 \text{ mT}$ )	10 h	parabolic	3 % (fine)

### Thermalization process

Nuclear demag cools down the nuclear spin ensemble. How does this couple to your sample?

Spin system has internal relaxation time  $\tau_2 \sim 0.1 \dots 10 \text{ ms}$  (fast)

Energy exchange between nuclear spins and conduction electrons is characterized by spin-lattice relaxation time  $\tau_1$ metals obey the Korringa law:  $\tau_1 = \kappa/T_e$ typically  $\kappa \sim 0.01 \dots 10$  sK when  $T_e \sim 50 \ \mu K \implies \tau_1 \sim 200 \ s \dots 200 \ ks \implies \tau_2$ 

THEREFORE  $T_e \neq T_n$ , conduction electrons may be much HOTTER than the nuclear spins

### NMR equations

Thermal equilibrium can be analyzed in terms of NMR relations

Magnetization relaxes as:

with

=>

towards equilibrium

1/1

¥.

$$\frac{dM}{dt} = -\frac{1}{\tau_1} (M - M_0)$$

$$M = -\frac{I+1}{3I} M_{sat} \frac{\mu B}{k_B T_n} \propto \frac{1}{T_n}$$

$$M_0 = -\frac{I+1}{3I} M_{sat} \frac{\mu B}{k_B T_e} \propto \frac{1}{T_e}$$

$$\frac{d}{dt} (\frac{1}{T_n}) = -\frac{1}{\tau_1} (\frac{1}{T_n} - \frac{1}{T_e})$$

$$\frac{dT}{dt} \ll \tau_1 = \kappa/T_1$$

Since 
$$\frac{d(1/T)}{dt} = -\frac{1}{T^2} \frac{dT}{dt} \& \tau_1 = \kappa/T_e$$
  
$$\implies \frac{dT_n}{dt} = (T_e - T_n) \frac{T_n}{\kappa}$$

### Warm up relations

Heat loads typically burden the conduction electrons, which eventually dump the heat to the nuclear spin system

Nuclei warm up as  $\frac{dT_n}{dt} = \frac{\dot{Q}}{C_B} = \frac{\mu_0 T_n^2}{V \lambda B_f^2} \dot{Q}$  $\implies \qquad \frac{T_e}{T_n} = 1 + \frac{\mu_0 \kappa \dot{Q}}{V \lambda B_f^2} = 1 + \frac{\dot{Q}}{\dot{Q}_n}$ where  $\dot{Q}_n = \frac{V \lambda B_f^2}{\mu_0 \kappa}$ 

is the "characteristic load", depending on the magnetic field  $B_f$ -  $T_e \sim T_n$  if  $\dot{Q} \ll \dot{Q}_n$ 

#### Characteristic load

For example

$$B_f = 50 \text{ mT}$$

$$n_{\text{Cu}} = 100 \text{ mol} \implies \dot{Q}_n = \frac{V \lambda B_f^2}{\mu_0 \kappa} \approx 0.7 \text{ }\mu\text{W}$$

$$\kappa_{\text{Cu}} = 1.2 \text{ sK}$$

For constant  $\dot{Q}$   $T_n^{-1}$  decreases linearly:

$$\frac{dT_n^{-1}}{dt} = -\frac{\mu_0 \dot{Q}}{V \lambda B_f^2} = -\frac{\dot{Q}}{\kappa \dot{Q}_n}$$

and so does  $T_e^{-1}$ 

$$\frac{dT_e^{-1}}{dt} = \frac{\dot{Q}_n}{\dot{Q} + \dot{Q}_n} \frac{dT_e^{-1}}{dt} = -\frac{\dot{Q}}{\kappa \left(\dot{Q} + \dot{Q}_n\right)}$$





Fig. 10.8. Temperatures, see (10.21), of the nuclear and electronic systems of Cu after demagnetization. The data show the warm-up rates, see (10.26), for the given molar heat leaks  $\dot{Q}/n$  to the Cu refrigerant in a final field  $B_{\rm f} = 7 \,\mathrm{mT}$  [10.10]

## Lowest possible $T_e$

Conduction electron temperature cannot be made arbitrarily low



Magnetic field, B [mT]

24

This is impractically low field for most purposes To maintain more heat capacity, field is usually kept larger (mind also that b = 0.34 mT for Cu)

# Heat leaks

Success or failure of nuclear demag is determined by heat leaks ...

- thermal conduction (support, electric leads, heat switch, ...) - thermal anchoring is crucial
- thermal radiation (radiation shield at T < 1 K)
- remnant gas in vacuum space ( $p_{\rm He} < 10^{-10}$  Pa)
- mechanical motion (pumps, boiling fluids, people, traffic, ...)
  - big mass (several tons)
  - flexible support (air springs, soft tubing, rubber fittings, ...)
- radioactivity & cosmic radiation
- electric and magnetic interference
  - passive & active shielding, filtering
- internal time-dependent heat leaks (e.g. H<sub>2</sub> ortho-para conversion)

#### Cryostat support



**Fig. 10.9.** Schematic diagram of a support system for a nuclear refrigeration cryostat. The cryostat is mounted on a concrete block (block A) supported by air springs. On top of block A are placed two smaller blocks (only one shown, block B) resting on thick pads of rubber which carry the wooden beams supporting the cryostat. The pumping tubes are, firstly concreted, into a massive block on the laboratory floor, to remove the vibrations of the pumps, secondly, taken through metal bellows, thirdly, concreted into the main block A, and finally led via a rubber section to be fixed to the sub-blocks B [10.10, 10.36]

# Typically one achieves 10 ... 50 pW/mol (best cases 5 ... 10 pW/mol)

### Double nuclear demagnetization

picokelvin installation at HMI in Berlin (operational from 1992 to 1996) Neutron diffraction on nuclear spin ordering in silver



2	
4He pot	
· · · ·	3
Oxford 600 dilution refrigerator	
	T <sub>min</sub> = 5 m
60Co NO thermometer	3 µW at 10
Heat switch; AI foils	R <sub>T</sub> = 18 K <sup>2</sup>
Pt-NMR thermometer	
	Runge -
Refrigerant magnet: 9 T	
	RRR = 900
Nuclear cooling stage:	T <sub>min</sub> = 50 )
Radiation shields	
	e-beam we
Thermal link: natural A o	BBB - 150
Polarization magnet; 7 T	$R_T = 4 K^2/$
Neutron beam path	
Sample I O O WAA	- KKR > 400

## Helsinki cryostat



# Refrigerating helium

Lancaster design: NS inside helium cell to overcome enormous Kapitza resistance between liquid He & metal coolant



### Low-temperature records

