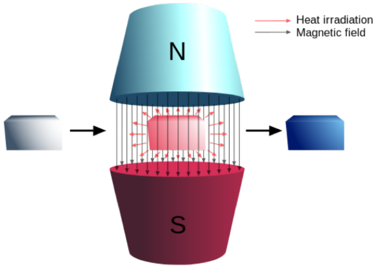
# Frustrated magnets and other cool materials

*theoretical prospectives and experimental examples*

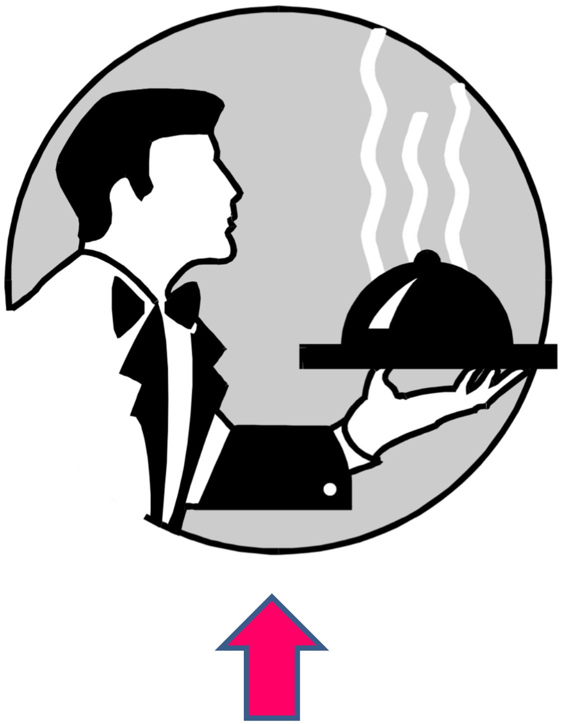
Mike Zhitomirsky

PHELIQS/IRIG/CEA



# Magnetic refrigeration in a nutshell

How to Order Entropy



in this talk

How to Control Entropy

credit to I. Hepburn

# Acknowledgments

C. Marin, J.-P. Brison, D. Braithwaithe, P. Dalmas de Reotier

(all Pheliqs/IRIG)

J.-M. Duval, D. Paixao (SBT/IRIG)

E. Lhotel (I. Néel)

A. Honecker (U. Cergy)

MATADIRE

**IRN-CNRS network « Strongly correlated electron systems as advanced magnetocaloric materials – SCESAMM »**

# Outline

- Magnetic refrigeration: old history - new motivations
- Physical principles
- Frustrated magnets
- $Yb_3Ga_5O_{12}$ – a new refrigerant material
- A few other examples

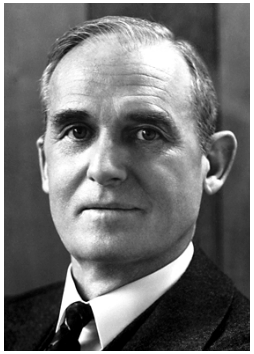
# History

- Cooling to mK temperatures by adiabatic demagnetization of paramagnets

  P. Debye (1926), W. Giauque (1927)

- First practical demonstration of ADR: Giauque and MacDougall (1933)

$$T_f = 0.53/0.34/0.25\text{K} \text{ from } T_i = 3.4/2.0/1.5\text{K}$$
$$\text{with } \Delta B = 0.8\text{T} \text{ using 61g of } Gd_2(SO_4)_3 \cdot 8H_2O$$



The Nobel Prize in Chemistry 1949
William F. Giauque

- ADR was principal subK refrigeration technique till 1960s

- Refrigeration technique for the upcoming Quantum Technology Revolution?

# Low-temperature magnetic cooling

- Ideal paramagnet: noninteracting dipoles with internal entropy

$$S_0 = k_B N \ln(2J+1)$$

  - look for materials with largest $J$

- Magnetic field aligns dipoles reducing their entropy

$$\hat{H} = -g\mu_B \mathbf{H}\cdot\mathbf{J} \quad \Rightarrow \quad S(H,T) = f(H/T)$$

- Adiabatic variations of temperature

$$T_f = T_i \frac{B_f}{B_i}$$

  - lowest temperature is reached as $B_f \to 0$

# Paramagnetic materials

P. Wikus *et al.* Cryogenics (2014)

Physical properties for some common paramagnetic refrigerants used in ADR (Carnot) cycles.

| Refrigerant | Chemical composition | $J$ (1) | $g$ (1) | $T_o$ (K) | $N$ (cm$^{-3}$) |
|---|---|---|---|---|---|
| CMN | $Ce_2Mg_3{\cdot}(NO_3)_{12}{\cdot}\ 24H_2O$ | 1/2 | 2 | 0.0015 | $1.65 \times 10^{21}$ |
| CCA | $CrCs\ (SO_4)_2{\cdot}12H_2O$ | 3/2 | 2 | 0.01 | $2.09 \times 10^{21}$ |
| CPA | $CrK\ (SO_4)_2{\cdot}12H_2O$ | 3/2 | 2 | 0.009 | $2.21 \times 10^{21}$ |
| FAA | $Fe\ (SO_4)_2NH_4{\cdot}12H_2O$ | 5/2 | 2 | 0.026 | $2.14 \times 10^{21}$ |
| MAS | $Mn\ (SO_4)_2(NH_4)_2{\cdot}6H_2O$ | 5/2 | 2 | 0.17 | $2.79 \times 10^{21}$ |
| DGG | $Dy_3Ga_5O_{12}$ | 15/2[a] | 8 | 400 | $1.28 \times 10^{22}$ |
| GGG | $Gd_3Ga_5O_{12}$ | 7/2 | 2 | 0.38 | $1.26 \times 10^{22}$ |
| GLF | $GdLiF_4$ | 7/2 | 2 | 0.48 | $1.34 \times 10^{22}$ |

- Improving efficiency, entropy capacitance
- Increased density/magnetic moments lead to stronger interactions and, hence, to entropy removal due magnetic ordering

➢ Not always - Frustrated magnets

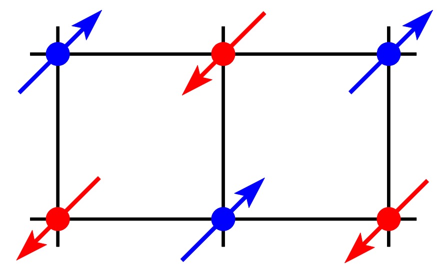
# Magnetic Frustration

Magnetic insulators with local moments (spins)

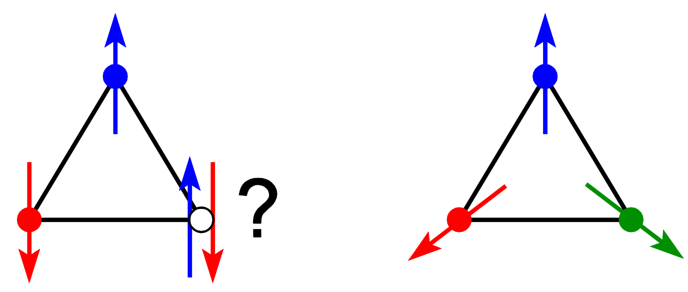
$$\hat{\mathcal{H}} = \sum_{\langle ij \rangle} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j - g\mu_B \mathbf{H} \cdot \sum_i \mathbf{S}_i$$

- direct exchange $J_{ij} < 0$; spins tend to align parallel ↑↑ :
  ferromagnetism
- superexchange $J_{ij} > 0$; spins tend to align antiparallel ↑↓ :
  antiferromagnetism

Néel order on square lattice : all bonds are satisfied

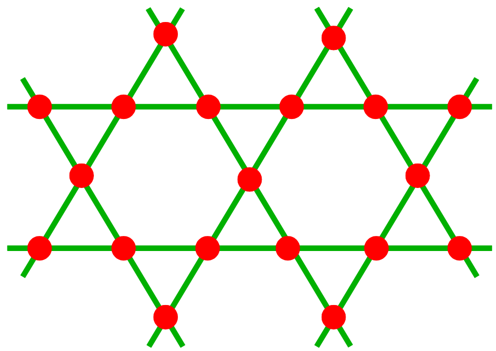


Geometrical frustration on triangular lattice

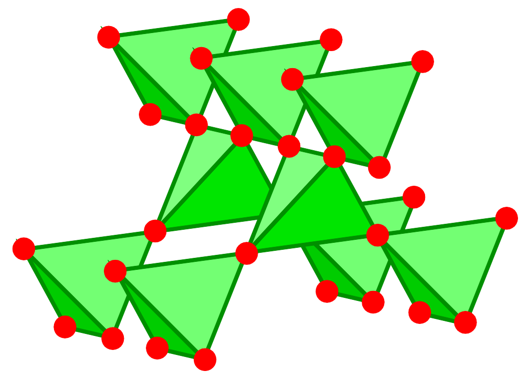


# Geometrically Frustrated Lattices

$ZnCu_3(OH)_6Cl_2$



kagomé

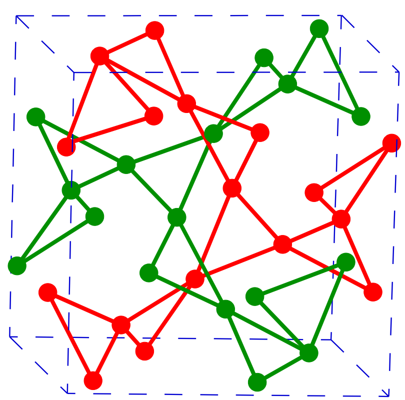


$Gd_2Ti_2O_7$

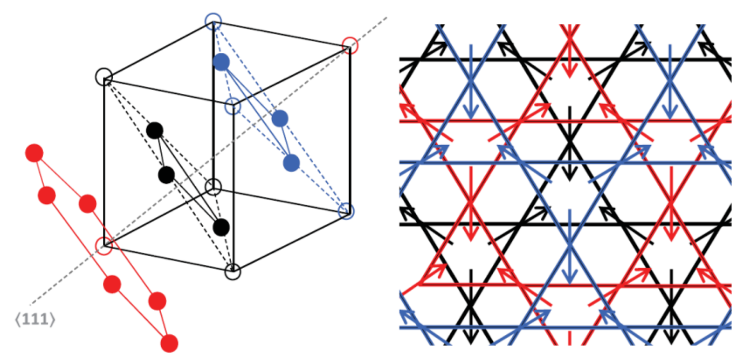
$ZnCr_2O_4$

pyrochlore

$Gd_3Ga_5O_{12}$



hyperkagomé (garnet)

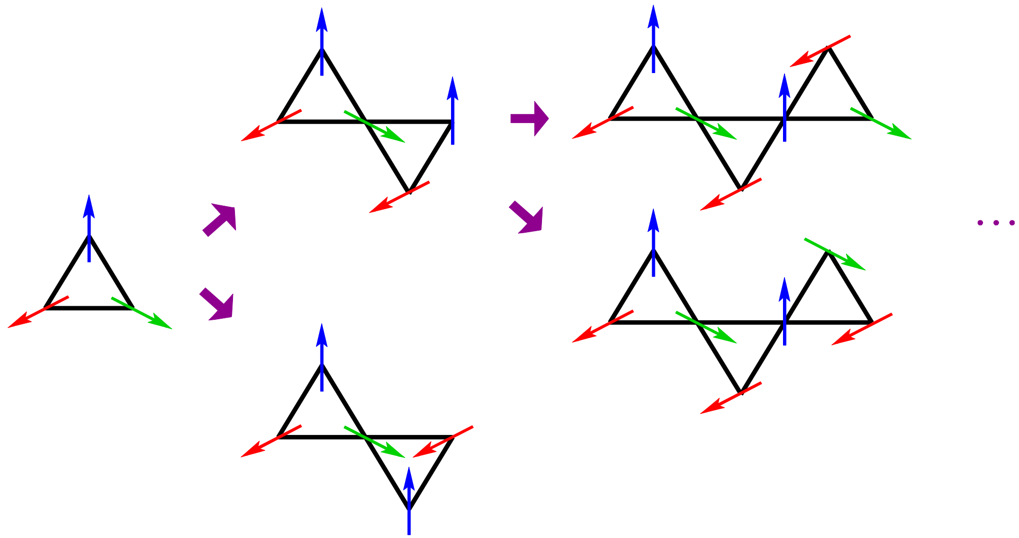



$IrMn_3$

fcc-kagomé

# Magnetic frustration: Degeneracy

- finite entropy in zero field: degeneracy between classical g.s.



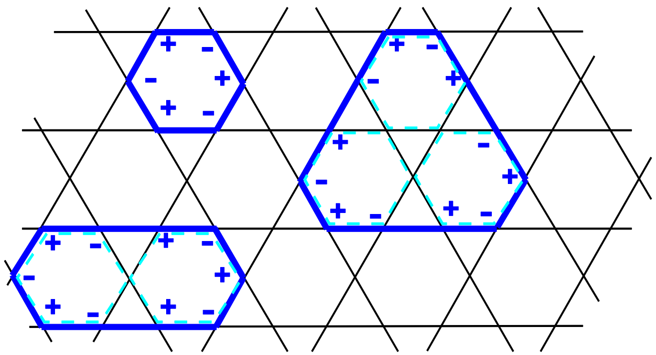
- infinite # of colorings

$$S_0 / N \approx 0.1264 k_B$$

- entropy persists up to the saturation field $H_{\text{sat}} \sim zJS$

- finite entropy at the saturation field: flat magnon bands

$$g\mu_B H_{\text{sat}} = 6JS\ (8JS)$$



$$S_0 / N \approx 0.1110 k_B \qquad \text{(kagome)}$$

$$S_0 / N \approx 0.1329 k_B \qquad \text{(pyro)}$$

Tsunetsugu & MZ, (2005,3007)

# Magnetic frustration

Competing Interactions
and/or
Frustrated Geometry

→

Large number of
degenerate low-energy
states

↓

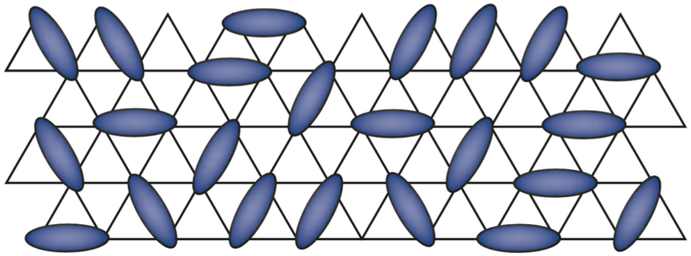
Persistent fluctuations

←

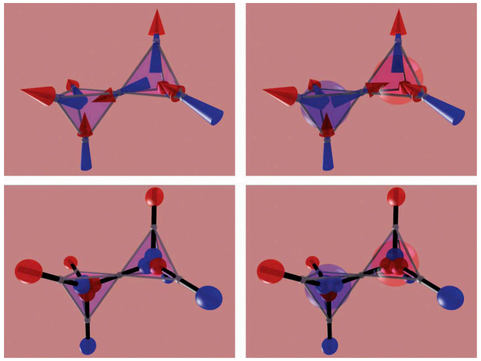
- Exotic phases
- Exotic excitations
- Macroscopic entropy
  (tunable by applied field)

# Exotic states in frustrated magnets

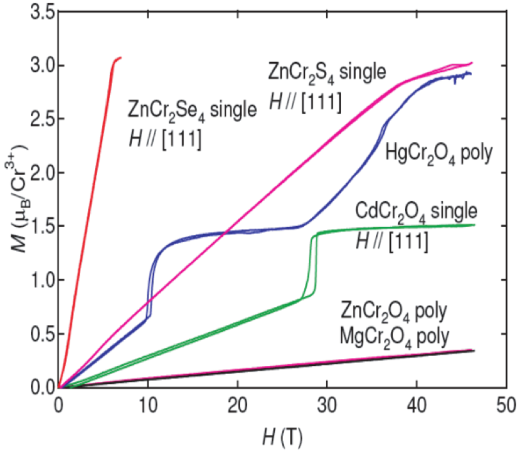
- Quanum spin liquids (RVB, Kitaev…)



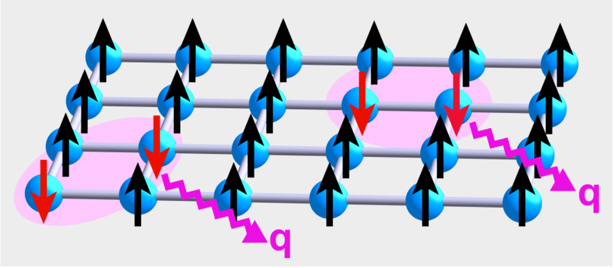
- Spin ice with  emergent monopoles



- Fractional magnetization plateaus




- Quanum spin nematic



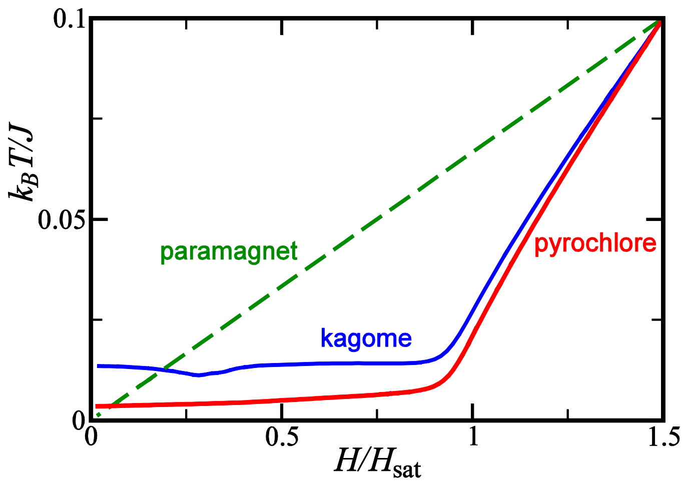
# Frustrated magnets for ADR

Delayed magnetic ordering and inherent degeneracy make frustrated magnets promising refrigerant materials

# MCE in frustrated magnets: theory

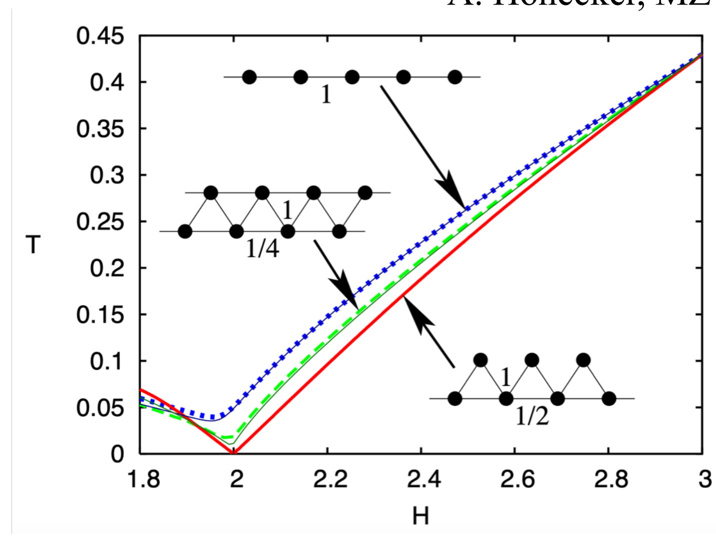
- Classical frustrated models

MZ (2003)



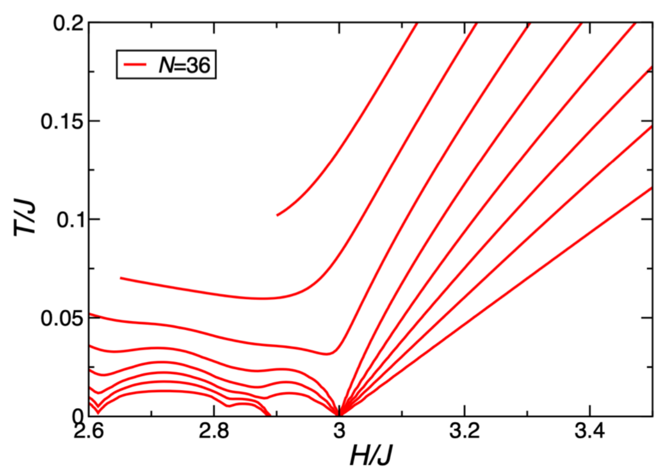

- spin-1/2, one-dimensional models

A. Honecker, MZ (2004)




- spin-1/2 kagome AF

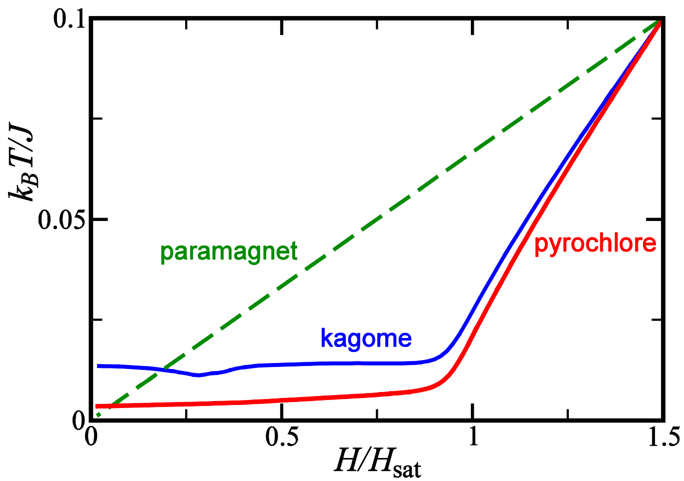
A. Honecker (2006)



# MCE in frustrated magnets: theory

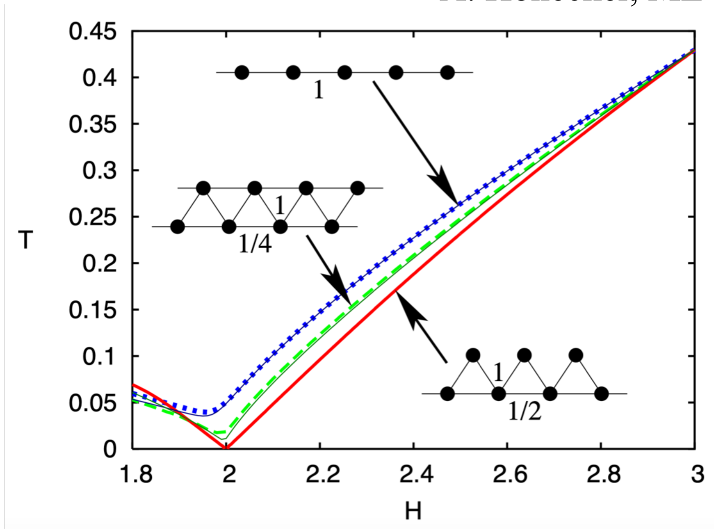
○ Classical frustrated models

MZ (2003)




○ spin-1/2, one-dimensional models

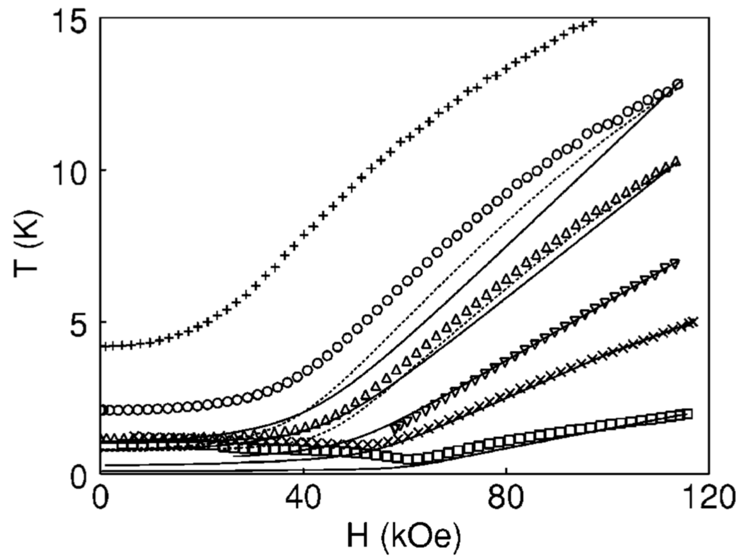
A. Honecker, MZ (2004)

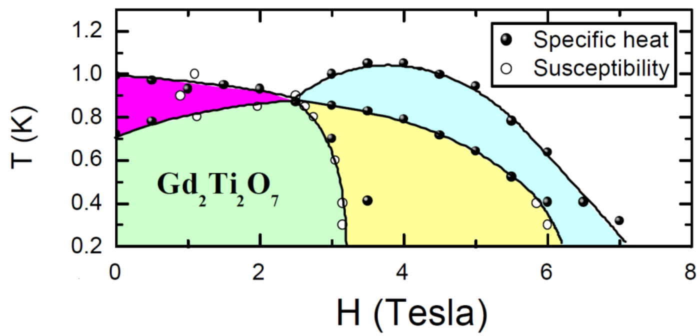



- $\Delta T_{\rm ad}$ is maximal towards the saturation field $H_{\rm sat} = zJS$
- Near $H_{\rm sat}$ entropy is accumulated in quasi-flat magnon bands
- Below $H_{\rm sat}$ further cooling may be precluded by residual interactions, quantum effects etc.

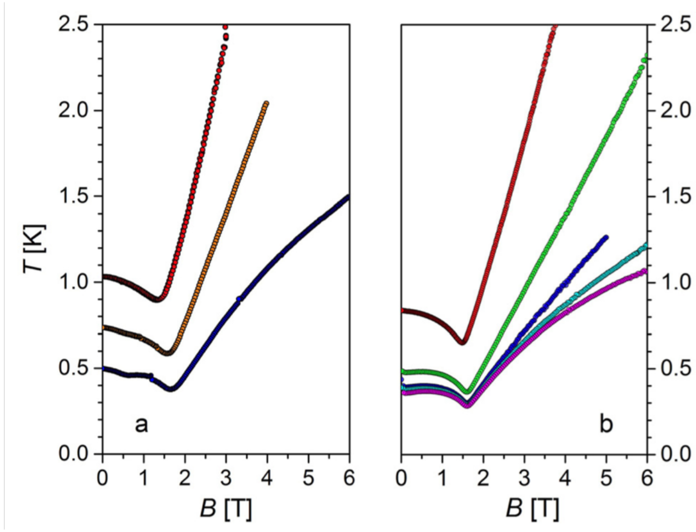
# MCE in pyrochlores $Gd_2Ti_2O_7$ and $Er_2Ti_2O_7$

- $Gd_2Ti_2O_7$ ($J = 7/2$), Sosin *et al* (2005)

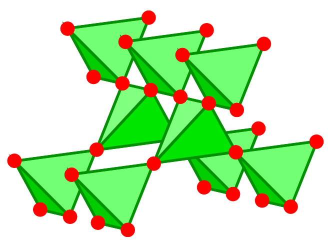



- $Er_2Ti_2O_7$ ($J = 1/2$), Wolf *et al* (2016)




➢ Fairly large $T_c \sim 1\mathrm{K}$ precludes their use for ADR in subK range



# MCE in pyrochlore $Dy_2Ti_2O_7$

- Spin ice material, Ising spins $(J = 1/2)$

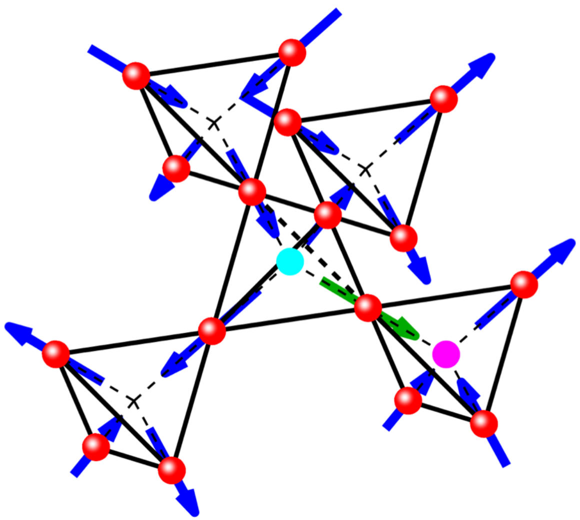
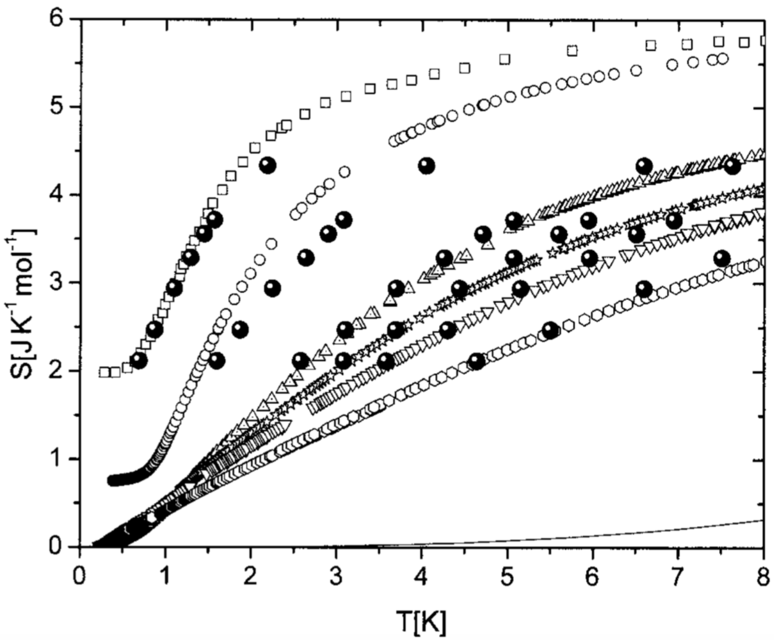


figure credit to P. Dalmas

- Orendac *et al* PRB, (2007)



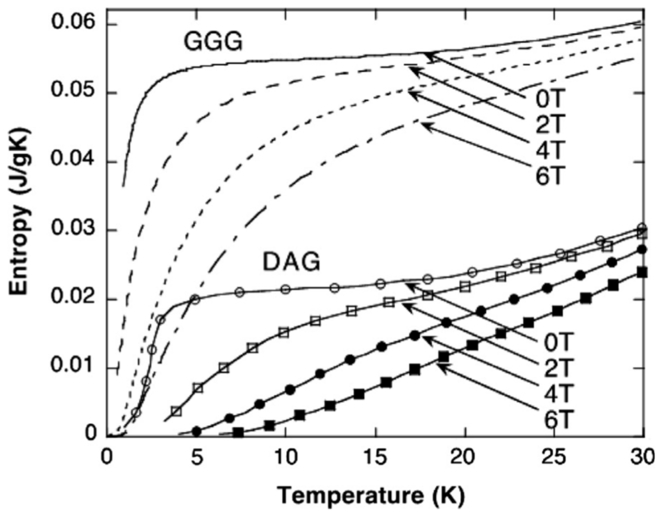

➢ residual entropy $S_{\rm ice} \approx \frac{1}{2} R \ln(3/2)$

➢ Spin freezing below $\sim 0.5\mathrm{K}$

# MCE in garnets $Gd_3Ga_5O_{12}$ and $Dy_3Al_5O_{12}$

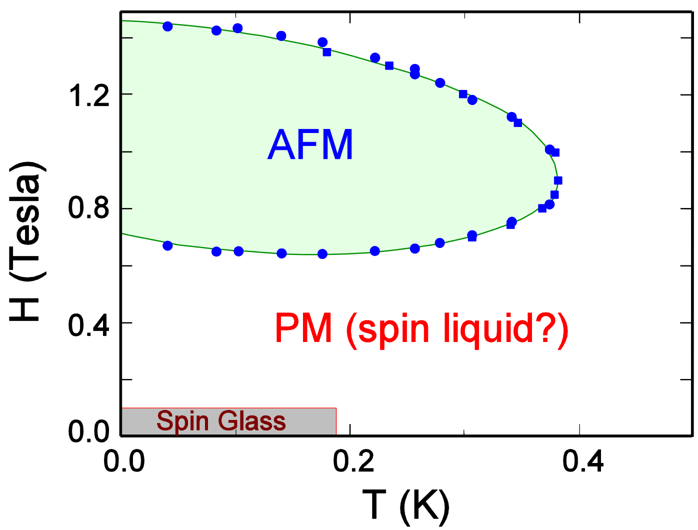
- Entropy diagram

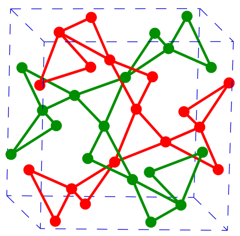
Wikus *et al,* (2014)




- Phase diagram of GGG,

Petrenko *et al,* (2002)



➢ Spin freezing below ~ 250mK

# **Garnet** $Yb_3Ga_5O_{12}$

- Effective spin $S = 1/2$, nearly isotropic *g*-tensor: 3.73, 3.60, 2.85
- favorable ion density $n_0 = 1.32 \cdot 10^{22}$ cm$^{-3}$ on frustrated hyperkagome lattice
- transition at $T_c = 54$mK, unknown magnetic state

Filippi *et al* (1980)

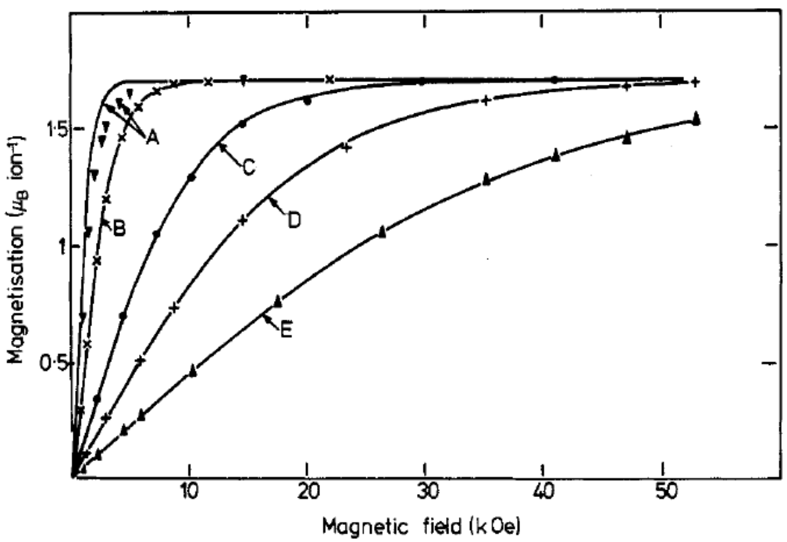
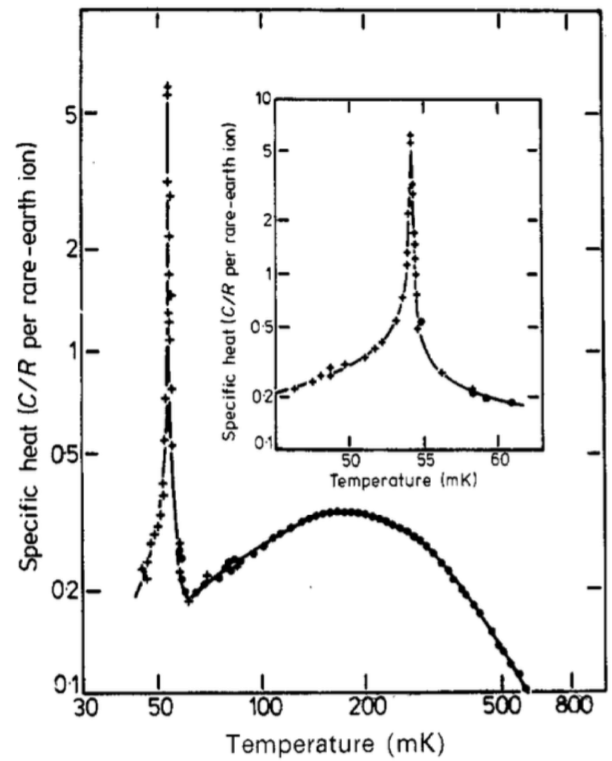



**Figure 3.** Magnetisation against applied field at various temperatures for YbGaG; $H \| [111]$. The experimental values are indicated by different types of points. A, 0·17 K; B, 0·38 K; C, 1·16 K; D, 2·17 K; E, 4·2 K. The full curves represent the calculations performed with an isolated ground-state doublet.




➢ ‘ideal paramagnet’ for $T = 1{-}4$ K (?)

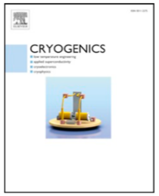
# Garnet $Yb_3Ga_5O_{12}$

Cryogenics 105 (2020) 103002

Contents lists available at ScienceDirect

Cryogenics

journal homepage: www.elsevier.com/locate/cryogenics




## YbGG material for Adiabatic Demagnetization in the 100 mK–3 K range

Diego Augusto Paixao Brasiliano[a,b], Jean-Marc Duval[a,*], Christophe Marin[c], Emmanuelle Bichaud[c], Jean-Pascal Brison[c], Mike Zhitomirsky[c], Nicolas Luchier[a]

PHYSICAL REVIEW B **104**, 024427 (2021)

Editors' Suggestion

## Spin dynamics of the quantum dipolar magnet $Yb_3Ga_5O_{12}$ in an external field

E. Lhotel,[1] L. Mangin-Thro,[2] E. Ressouche,[3] P. Steffens,[2] E. Bichaud,[4] G. Knebel,[4] J.-P. Brison,[4] C. Marin,[4] S. Raymond,[3,*] and M. E. Zhitomirsky[4,†]

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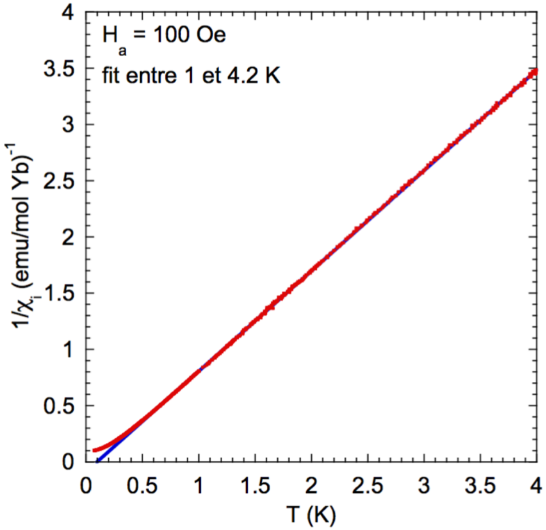
[4]*Univ. Grenoble Alpes, Grenoble INP, CEA, IRIG, PHELIQS, 38000 Grenoble, France*

# Curie-Weiss temperature in $Yb_3Ga_5O_{12}$




$$\frac{1}{\chi} = -0.087 + 0.893T \qquad \theta_{CW} = 97.4\text{mK}$$

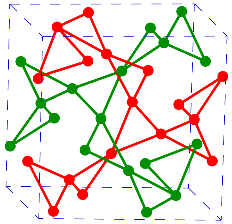
$$\mu_{eff} = g_{av}\sqrt{S(S+1)} \approx 2.6\mu_B \text{ vs. } 3\mu_B$$

$$D^{zz}(0) = \frac{\mu_0}{4\pi}\frac{(g\mu_B)^2}{a^3}\sum_{i,j}\left(\frac{1}{r_{ij}^3} - \frac{3z_{ij}^2}{r_{ij}^5}\right)$$

- Dipole contribution

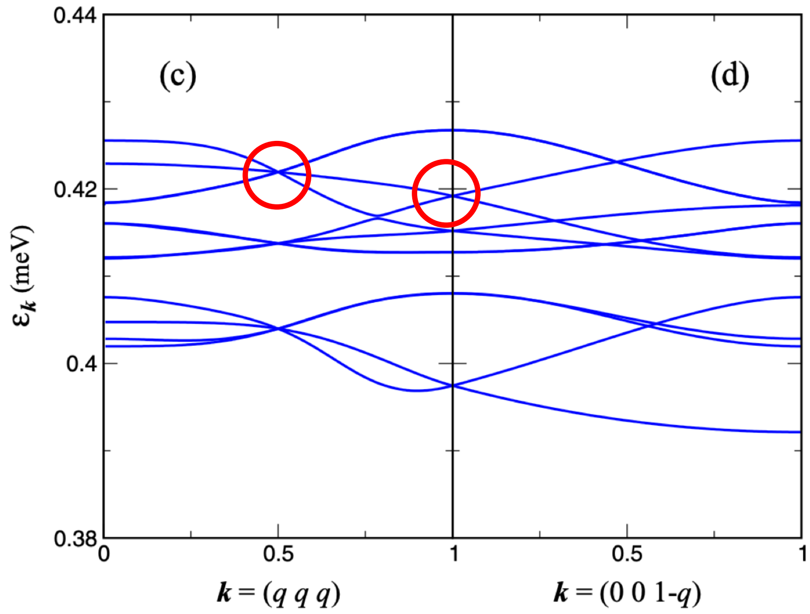
$$\theta_{CW}^{\text{dip}} = -\tfrac{1}{3}S(S+1)D^{zz}(0) \approx 101.4\,\text{mK}$$

➢ quantum $S = 1/2$ dipolar magnet on 3D kagome lattice



# Magnon dispersion in $Yb_3Ga_5O_{12}$

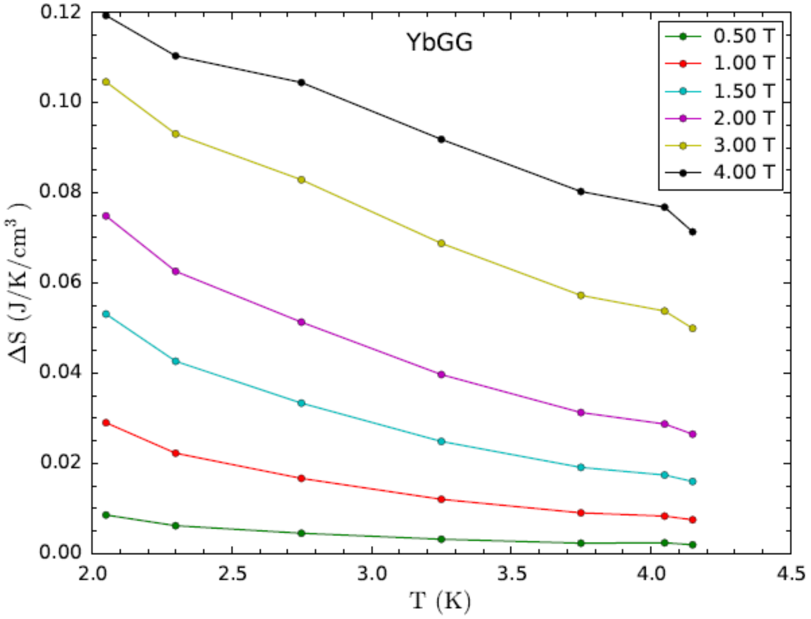
- Magnetic field $H = 2\mathrm{T}$




➢ Dirac and Weyl crossing points, topological magnon bands

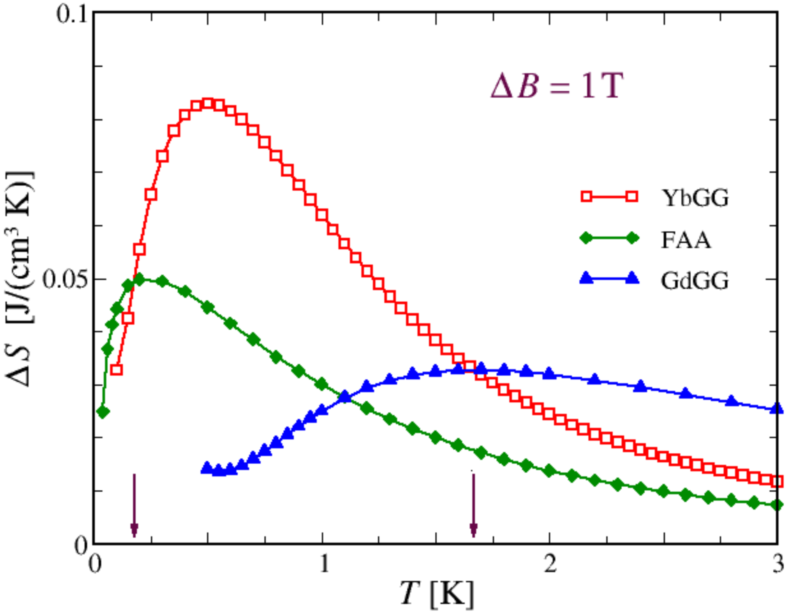
# MCE in $Yb_3Ga_5O_{12}$

- Entropy variations



# MCE in $Yb_3Ga_5O_{12}$

- Entropy variations from $M(T, B)$

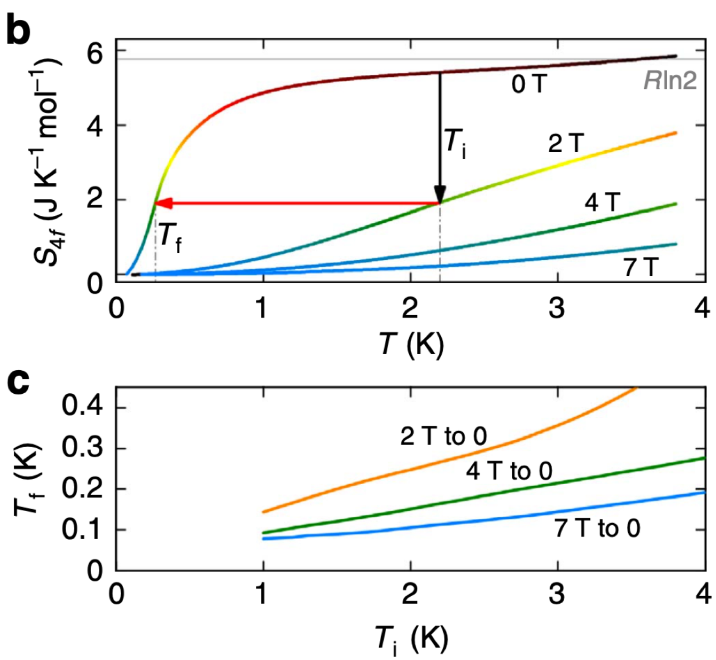



➢ Superior over standard refrigerant materials for $0.2 < T < 1.8$ K

# Ytterbium intermetallics

## Large magnetocaloric effect and adiabatic demagnetization refrigeration with $YbPt_2Sn$

Dongjin Jang[1], Thomas Gruner[1], Alexander Steppke[1], Keisuke Mitsumoto[2], Christoph Geibel[1] & Manuel Brando[1]




IOP Publishing
Journal of Physics: Condensed Matter
J. Phys.: Condens. Matter **26** (2014) 485002 (10pp)
doi:10.1088/0953-8984/26/48/485002

**Unusual weak magnetic exchange in two different structure types: $YbPt_2Sn$ and $YbPt_2In$**

T Gruner[1], D Jang[1], A Steppke[1], M Brando[1,2], F Ritter[3], C Krellner[3] and C Geibel[1]

- low $T_m$ = 250 & 180 mK due to weak magnetic interactions
- good heat conduction due to metallicity

**Table 1 | Comparison of parameters for various magnetocaloric materials.**

| | $J_{GS}$ | $g$ | $T_m$ (mK) | $d$ (g cm$^{-3}$) | $S_v$ (J K$^{-1}$ cm$^{-3}$) |
|---|---|---|---|---|---|
| CPA[23] | 3/2 | 2 | 10 | 1.83 | 0.042 |
| FAA[24] | 5/2 | 2 | 30 | 1.71 | 0.052 |
| GGG[25] | 7/2 | 2 | 800 | 7.10 | 0.363 |
| DGG[7,26] | 1/2 | –* | 400 | 7.30 | 0.123 |
| $YbPt_2Sn$ | 1/2 | 5.6 | 250 | 14.6 | 0.127 |

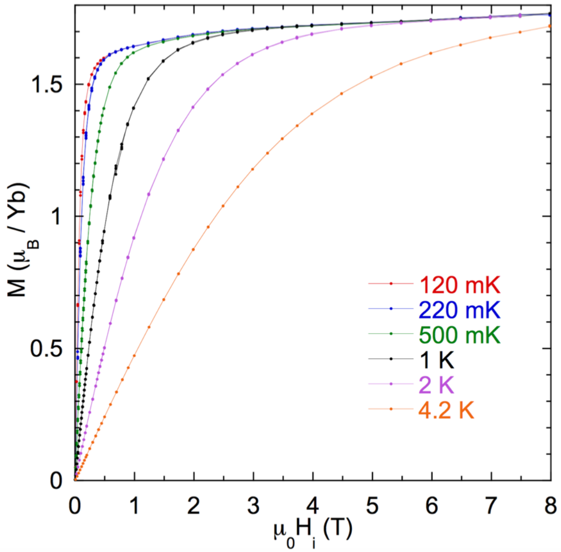
# Summary

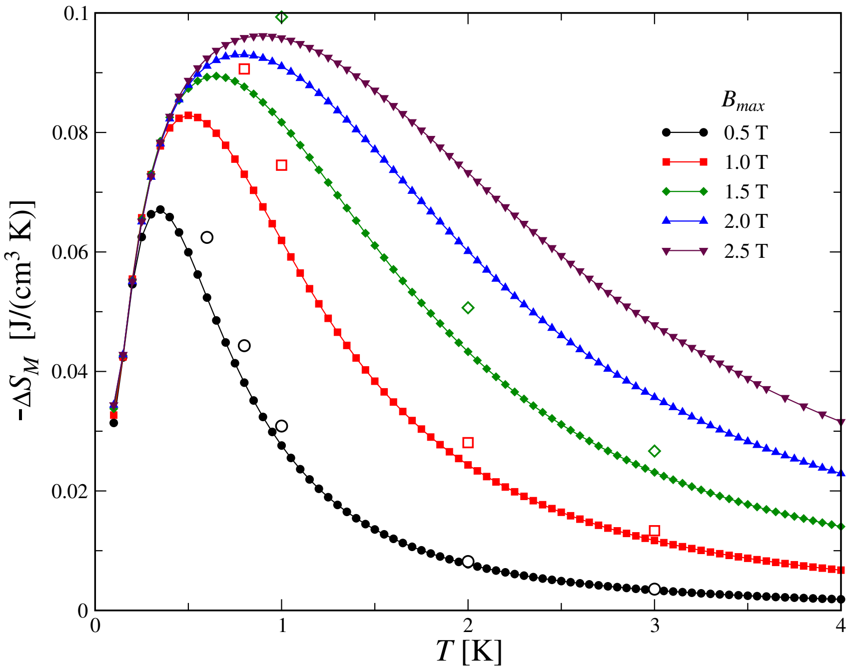
- New types of refrigerant materials for low-$T$ ADR:
  collective effects in frustrated and quantum magnets
- Not only large $J$ materials!
- Strongest cooling in a finite field $H^*$ (useful for multi-stage coolers?)
- New prominent examples $Yb_3Ga_5O_{12}$, Yb-intermetallics, $GdLiF_4$, $Ba_2GdSbO_6$ ; also interesting from the fundamental prospective

# Frustrated garnet $Yb_3Ga_5O_{12}$

- Entropy variations from $M(T, B)$

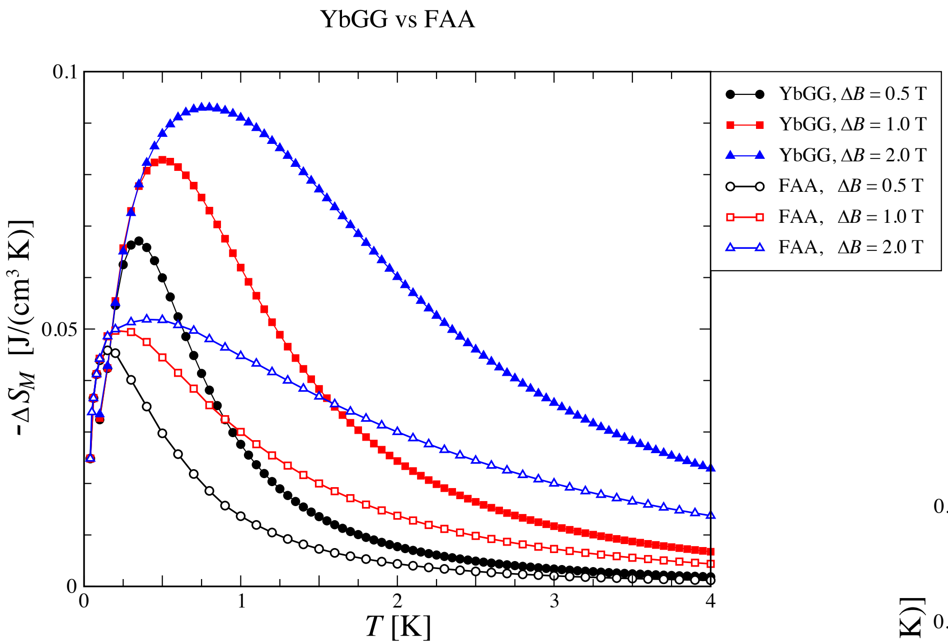
E. Lhotel *et al*



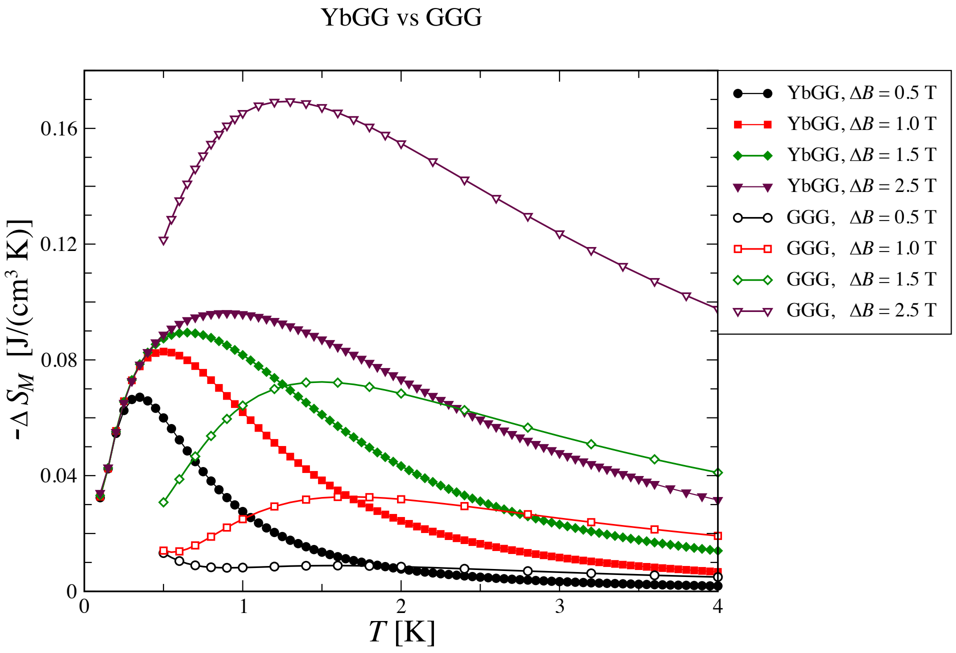



# Frustrated garnet $Yb_3Ga_5O_{12}$

- YbGG vs paramagnetic salt FAA :

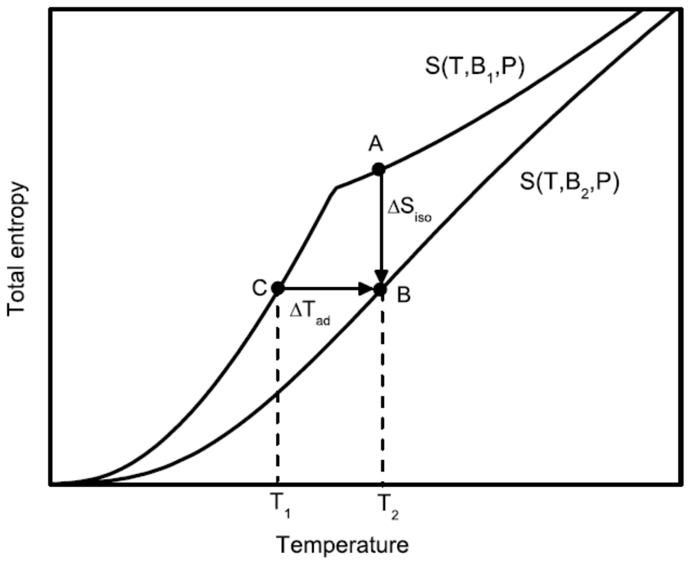



- YbGG vs GGG :



# Magnetocaloric Effect

- Reversible temperature changes induced by applied field
- Basic characteristics




- adiabatic temperature drop

$$\Delta T_{\mathrm{ad}} = \int_{B_i}^{B_f} \left( \frac{\partial T}{\partial B} \right) dB$$

- isothermal entropy variation

$$\Delta S_{\mathrm{iso}} = \int_{B_i}^{B_f} \left( \frac{\partial S}{\partial B} \right) dB$$

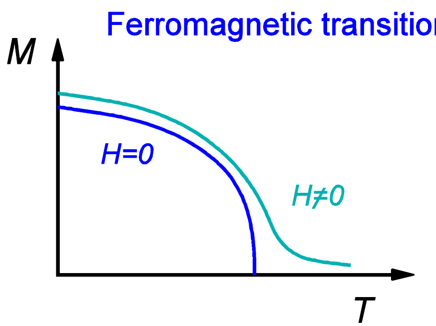
- Maxwell's relations

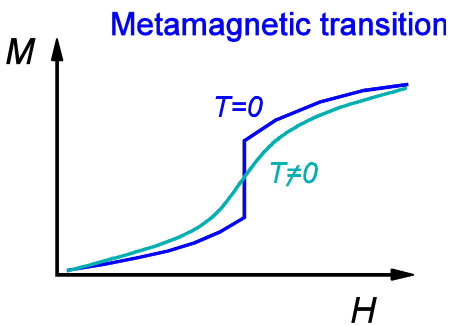
$$\Gamma_B = \frac{1}{T} \left( \frac{\partial T}{\partial B} \right)_S = -\frac{(\partial S/\partial B)_T}{C} \qquad \left( \frac{\partial S}{\partial B} \right)_T = \left( \frac{\partial M}{\partial T} \right)_B$$

# Magnetocaloric Effect

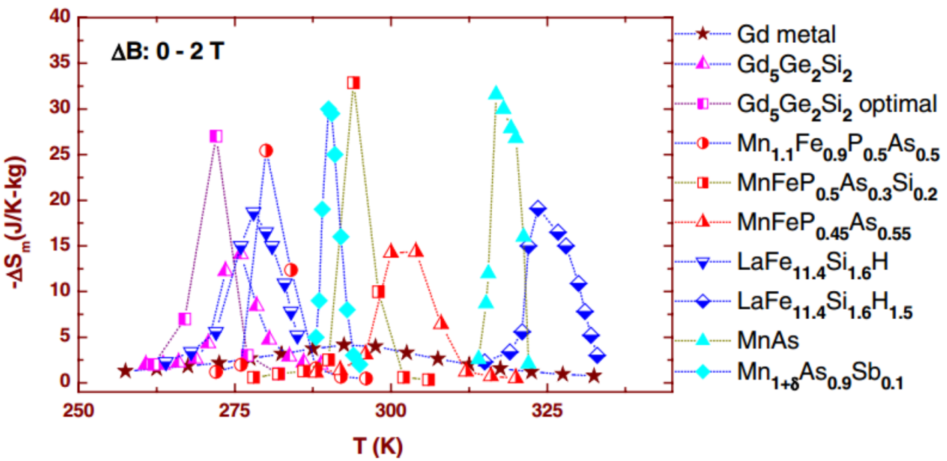
- MCE is enhanced near phase transitions

$$\left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial M}{\partial T}\right)_B$$




- Room temperature refrigeration with suitable FM materials




Gutfleisch *et al* (2011)