Title: Absence of Pauling's Residual Entropy in Dy2Ti2O

Date: Apr 25, 2013 02:30 PM

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Abstract: The discovery of the spin-ice phase in Dy2Ti2O7 numbers among the most significant findings in magnetic materials in over a decade. The spin-ice model is based on an elegant analogy to Paulingâ€™s model of geometrical frustration in water ice, and predicts the same residual entropy, as confirmed by numerous measurements. Melko, den Hertog and Gingras, with numerical work using a loop algorithm to speed up equilibration times, were able to determine an ordering for this system. This had not been seen experimentally observed by several groups. I will present new experimental results for the specific heat of Dy2Ti2O7, demonstrating why previous measurements were unable to correctly capture its low temperature behaviour. By carefully tracking the flow of heat into and out of the material, we observe a non-vanishing specific heat at low temperatures indicating the residual entropy does not actually agree with the Pauling value.

The Group at Waterloo

David Pomaranski

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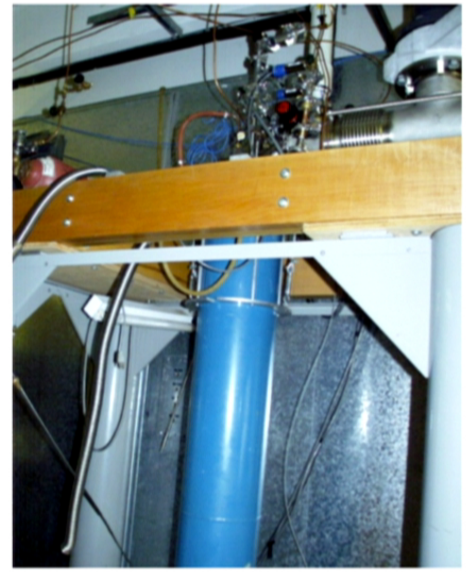
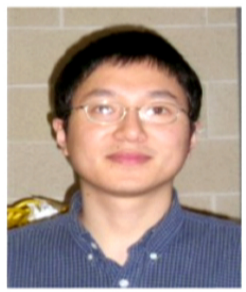


Jeff Mason



Shuchao Meng

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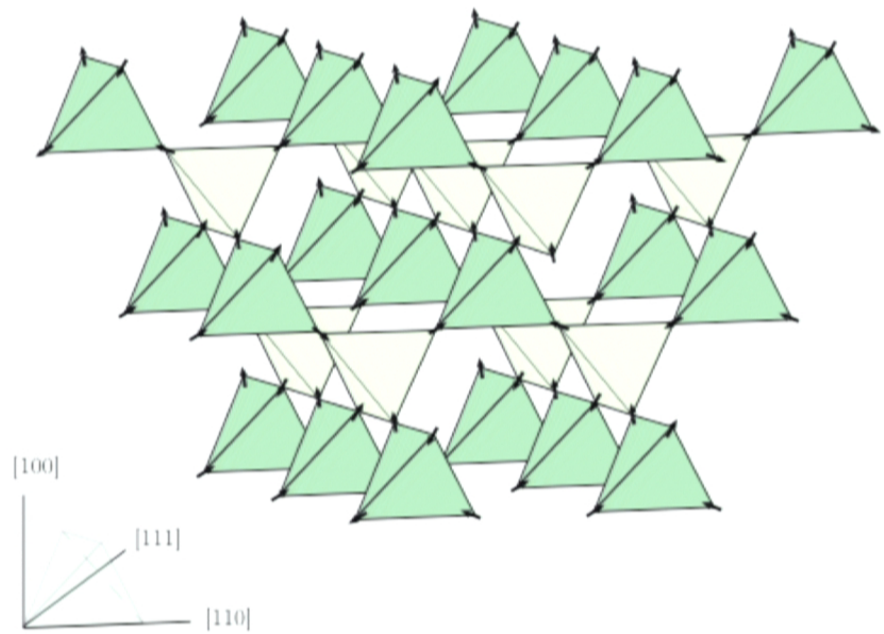
The material, $Dy_2Ti_2O_7$

- ***Interesting because***: magnetic analogue of water ice, magnetic monopole excitations!
- Pyrochlore lattice → Dy (magnetic) ions on corners
- Below 10 K spins are Ising along local <111> axes
- Can be modelled with FM NN exchange interaction

$$H = -J \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j$$

- 2-in-2-out ground state → Bernal & Fowler ice rules → residual entropy



Harris et al. PRL 1997, Ramirez et al. Nature 1999

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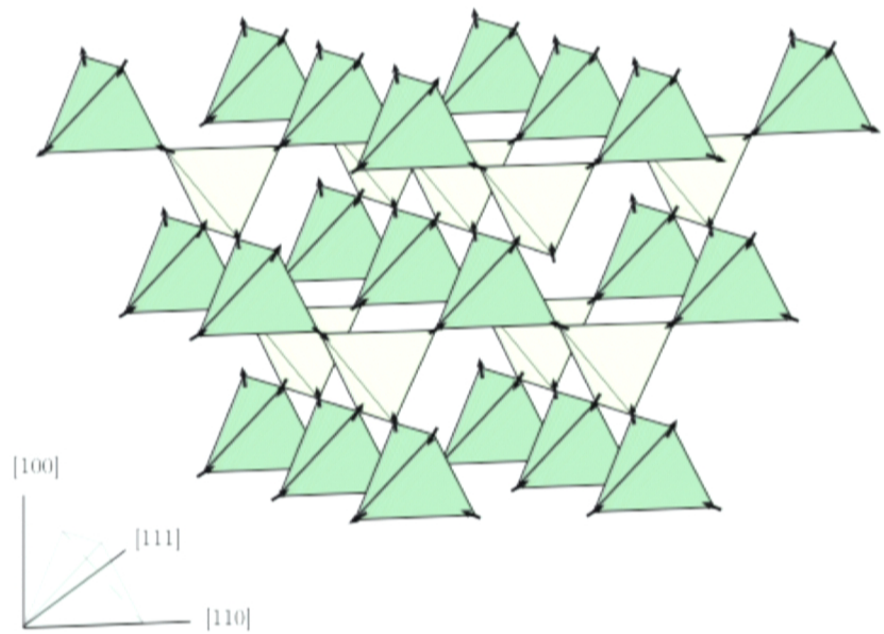

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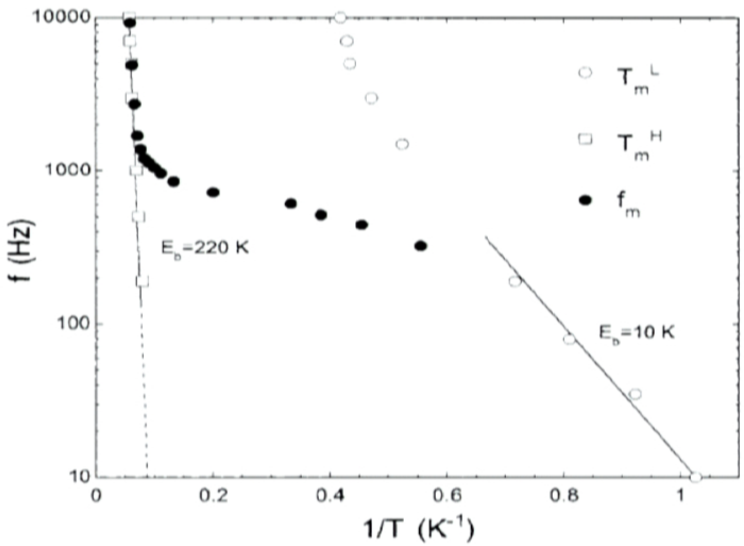
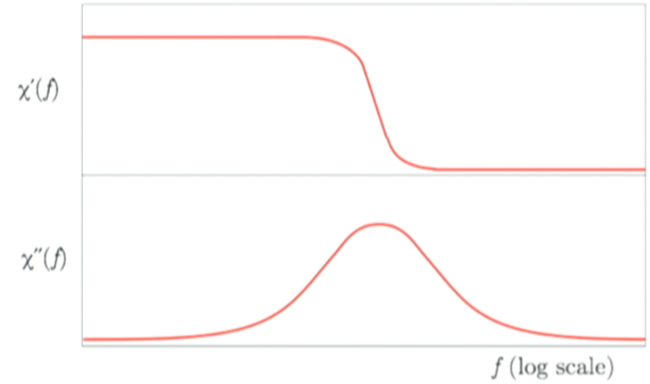
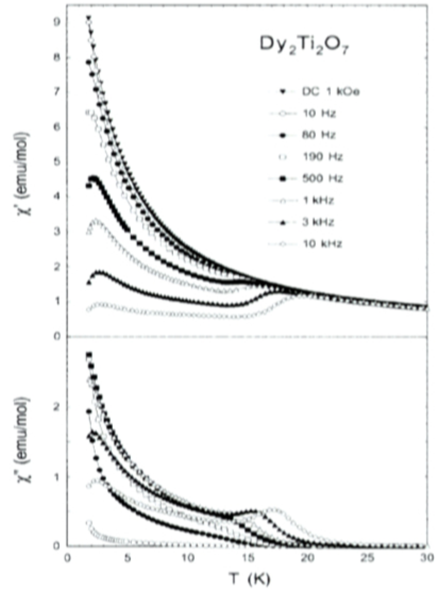
Early Susceptibility Measurements

Matsuhira, Hinatsu, Sakakibara
Journal of Physics, Condensed Matter (2001)







Somewhat similar parallel result:

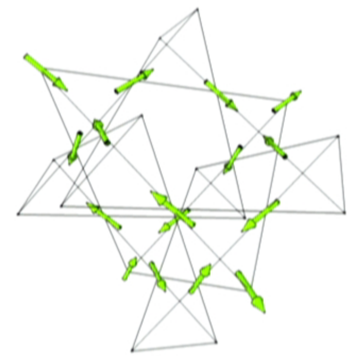
J. Snyder, J. S. Slusky, R. J. Cava, and

P. Schiffer, Nature (2001)

Dipolar spin ice model

$$H = -J \sum_{<ij>} \mathbf{S}_i^{z_i} \cdot \mathbf{S}_j^{z_j} + D r_{nn}^3 \sum_{j>i} \frac{\mathbf{S}_i^{z_i} \cdot \mathbf{S}_j^{z_j}}{|\mathbf{r}_{ij}|^3} - \frac{3(\mathbf{S}_i^{z_i} \cdot \mathbf{r}_{ij})(\mathbf{S}_j^{z_j} \cdot \mathbf{r}_{ij})}{|\mathbf{r}_{ij}|^5}$$

exchange term   dipolar term

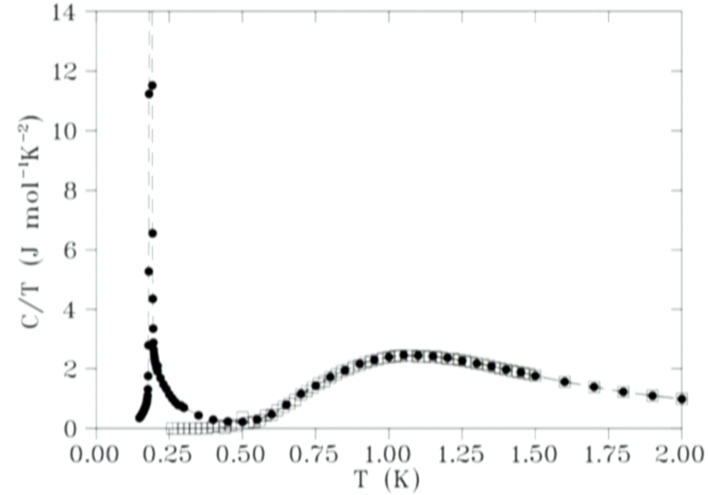


NN effective exchange model:

$$H = -J_{\text{eff}} \sum_{\langle i,j \rangle} \mathbf{S}_i^{z_i} \cdot \mathbf{S}_j^{z_j}$$

$$J_{\text{eff}} = J_{nn} + D_{nn}$$

FM +1.11 K   AFM -1.24 K   FM +2.35 K



den Hertog and Gingras PRL 2000,
Melko, den Hertog, Gingras PRL 2001
Bramwell and Gingras Science 2001
Yavors'kii et al. PRL 2008

Using loop algorithm, *Melko, den Hertog, Gingras* predict a low temperature ordered state (MDG state?)

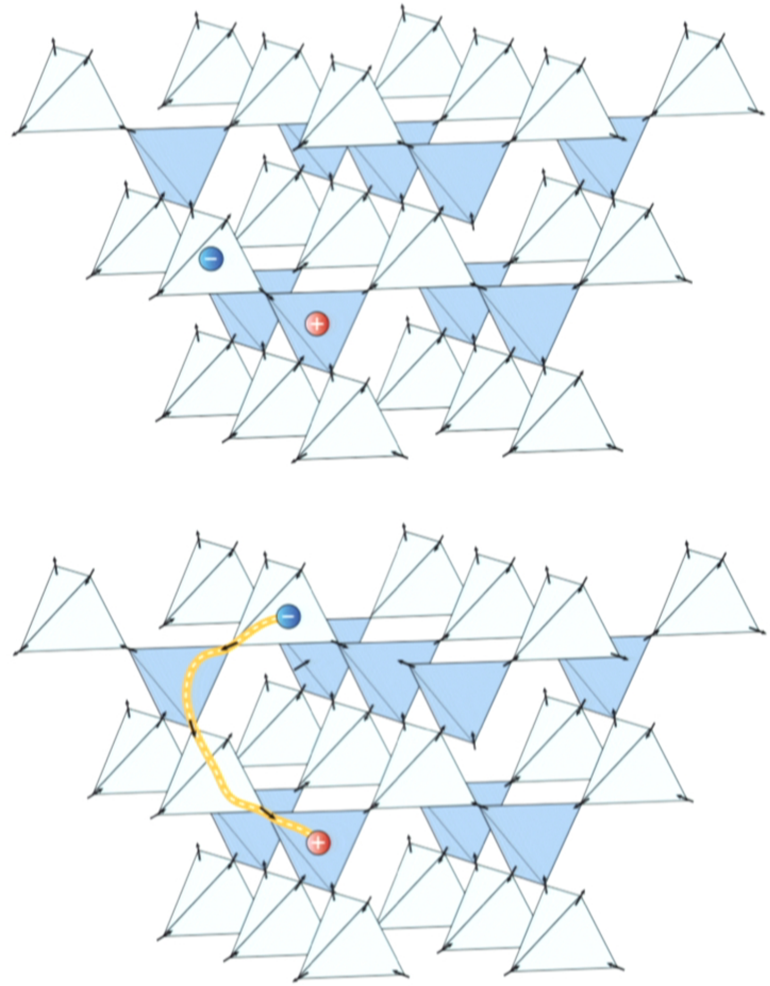
- Spin flipped out of the 2-in-2-out ground state

- Single spin flip creates two excitations of equal and opposite charge

- Can be viewed as magnetic monopoles

- The monopole pair can travel apart through subsequent spin flips

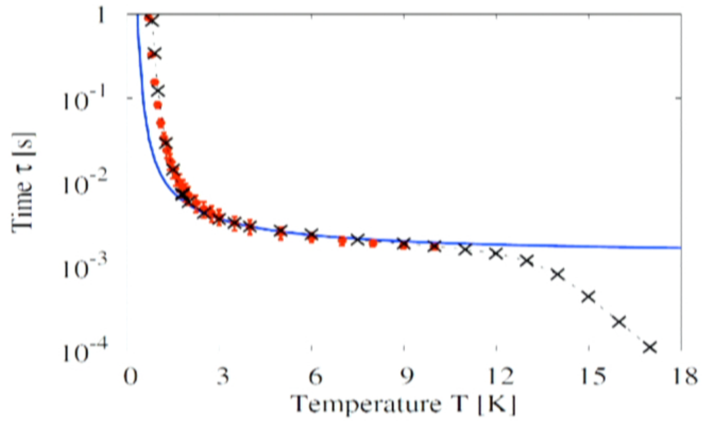
- Separation has zero energy cost in NN model - through screening they become de-confined

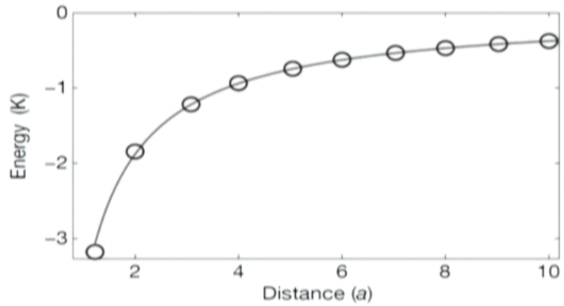


Drawing based on a figure from: Gingras, Science Vol. 326 (375), 2009

Monopole Picture

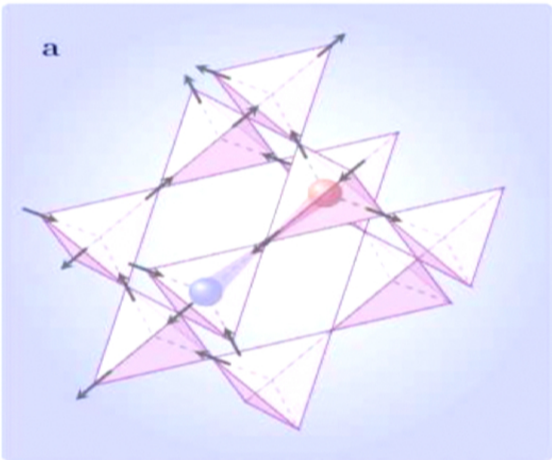
- Work by Jaubert and Holdsworth interpret features in measurements by Snyder et al. as signatures of monopole-like excitations in spin ices.
- Two-in two-out can be seen as a vacuum
- Three-in one-out (three-out one-in) can be seen as a quasi-particle (monopole).
- Magnetic charges behave as a Coulomb gas of monopoles.





Castelnovo, Moessner, Sondhi, Nature (2008).
Jaubert and Holdsworth, Nature Physics, (2009).

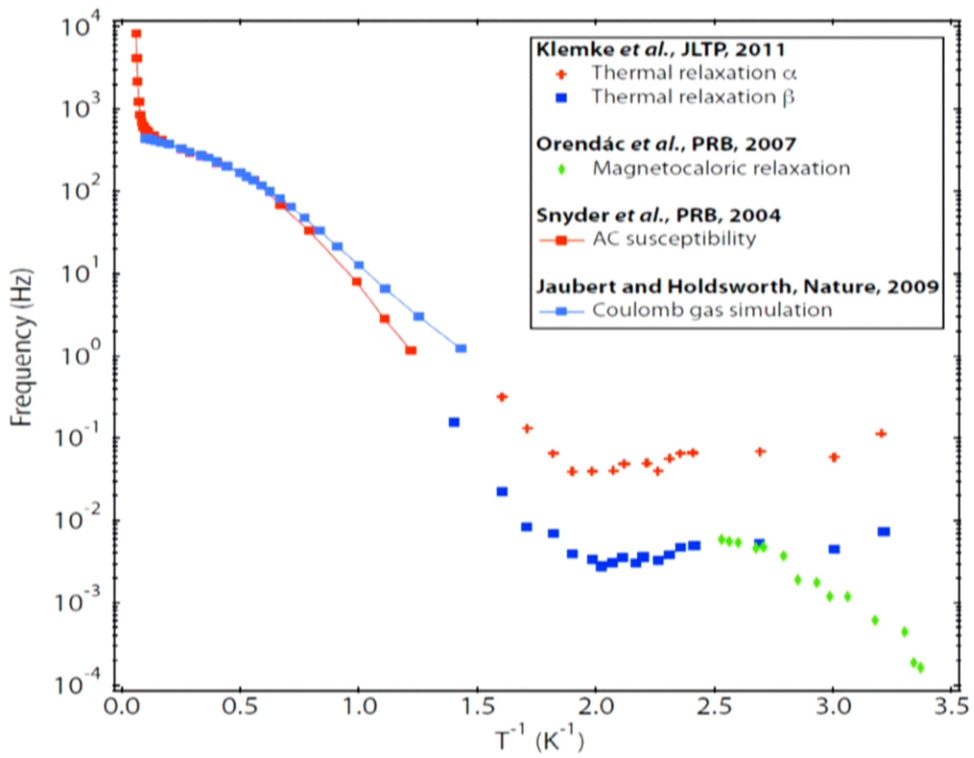
Ryzhkin in JETP 101, 481 (2005).



Thermal measurements

Thermal measurements obtain lower frequency relaxation rates

See strange
low temperature behaviour



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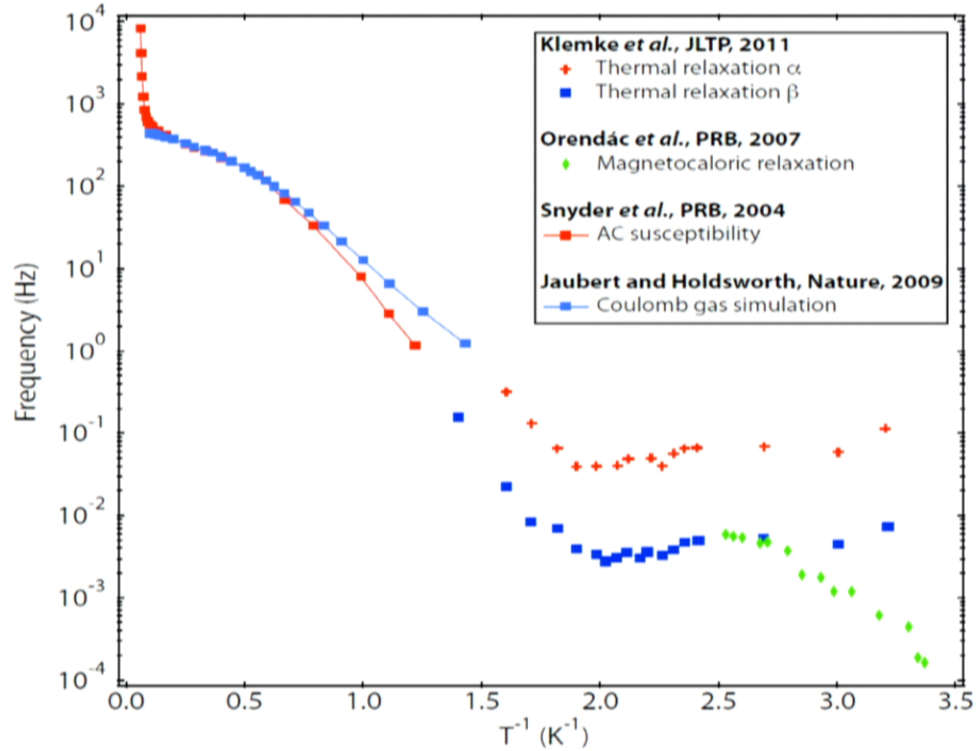

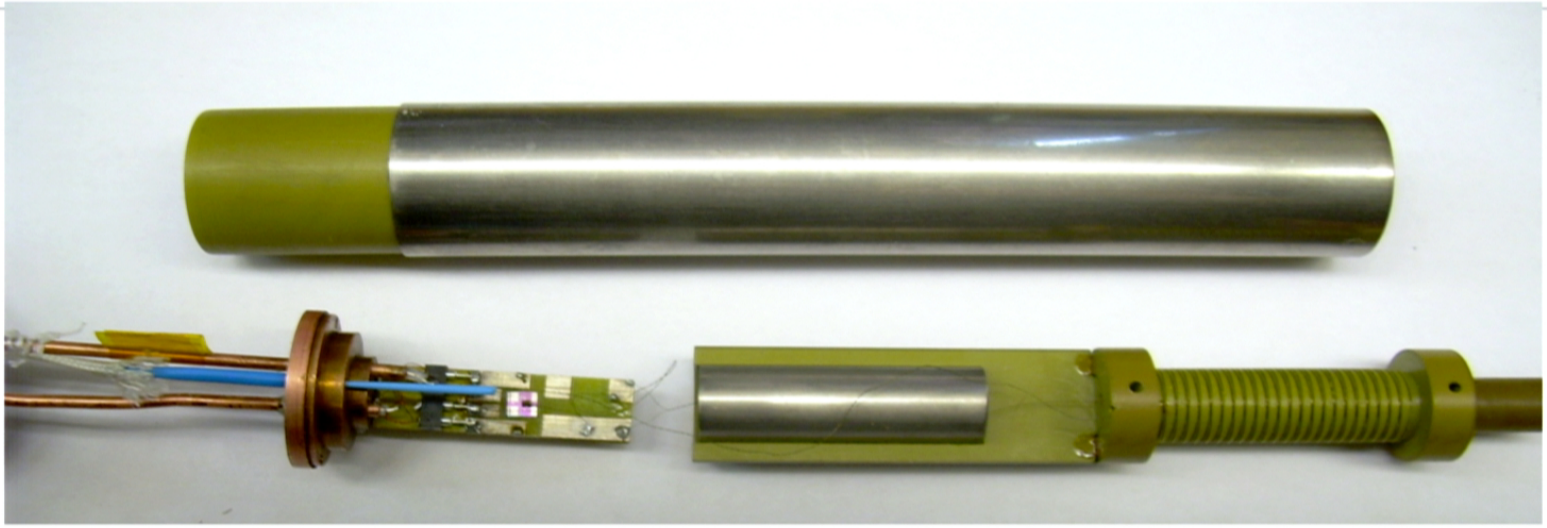

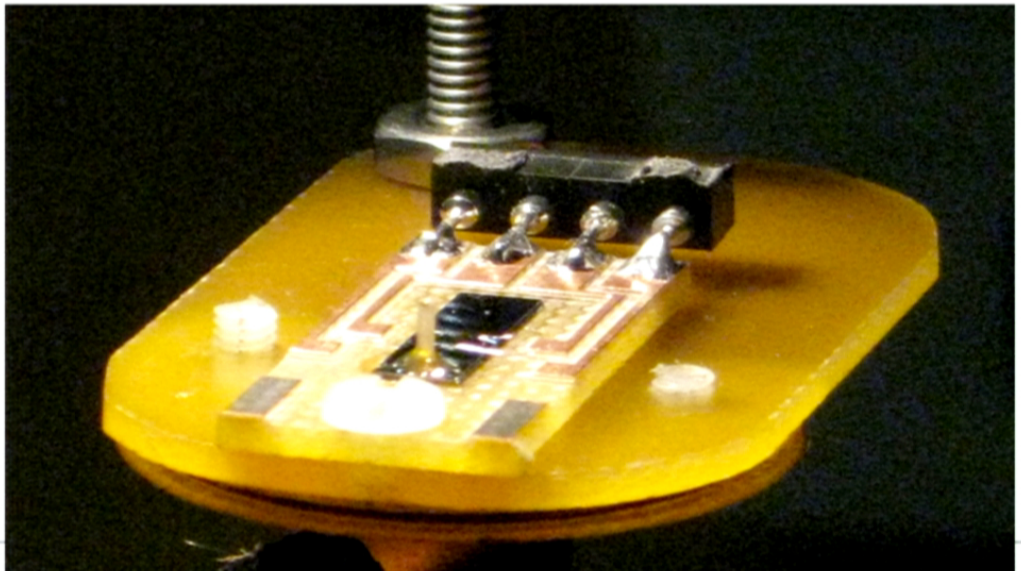

ac susceptibility measurement results for DTO

$$f(T) = f_o \exp\left(-E_B/kT\right)$$
$$\tau(T) = \tau_o \exp\left(E_B/kT\right)$$
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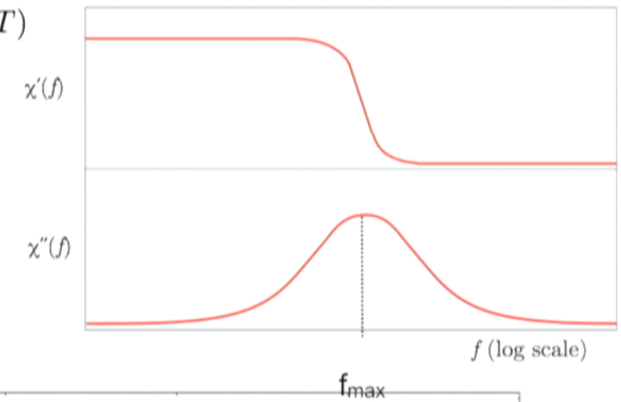
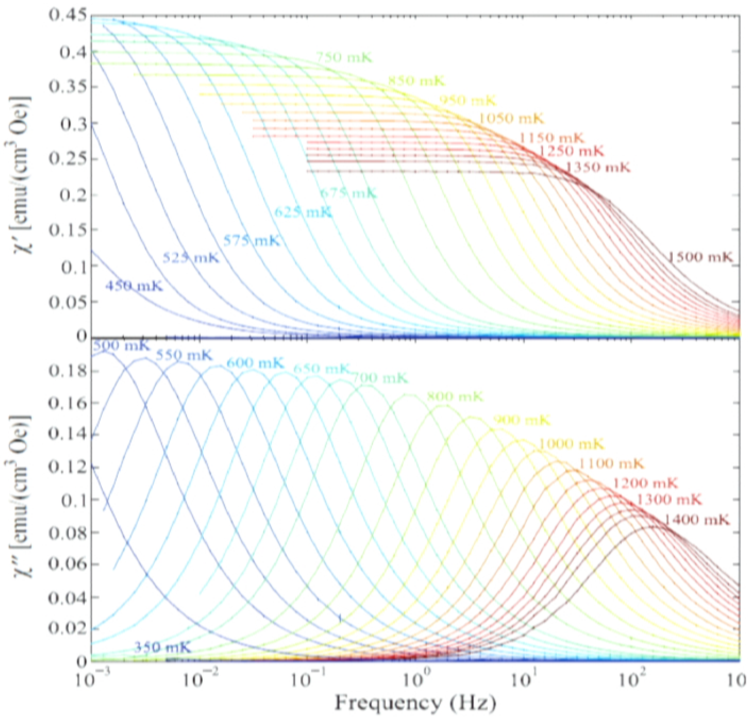
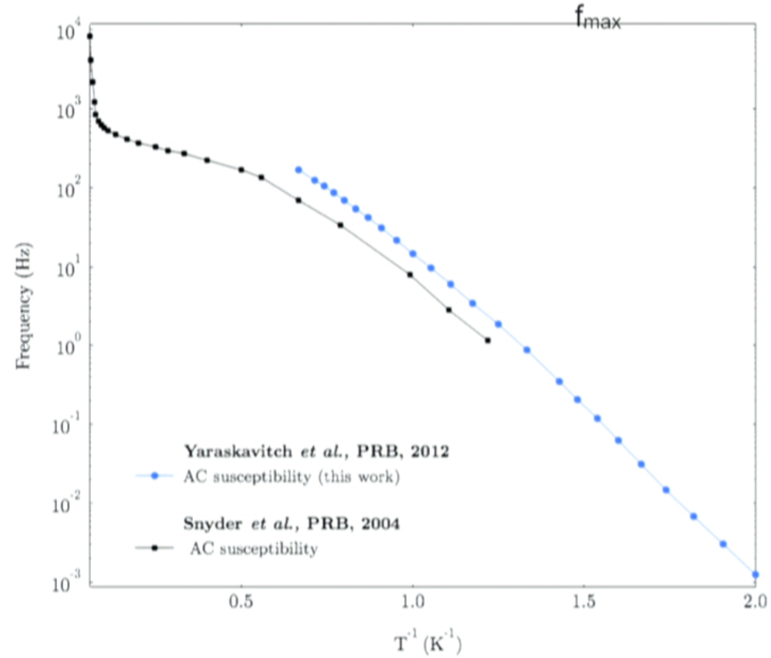


- Measures the relaxation time of the magnetic spins





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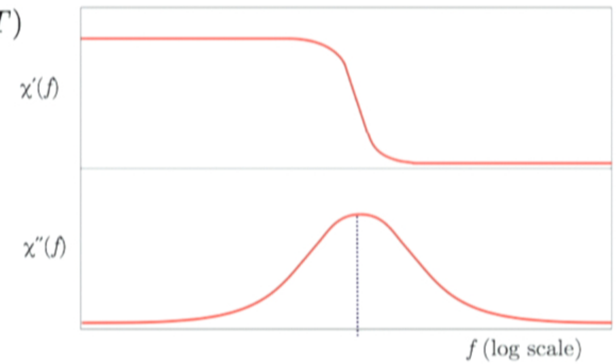

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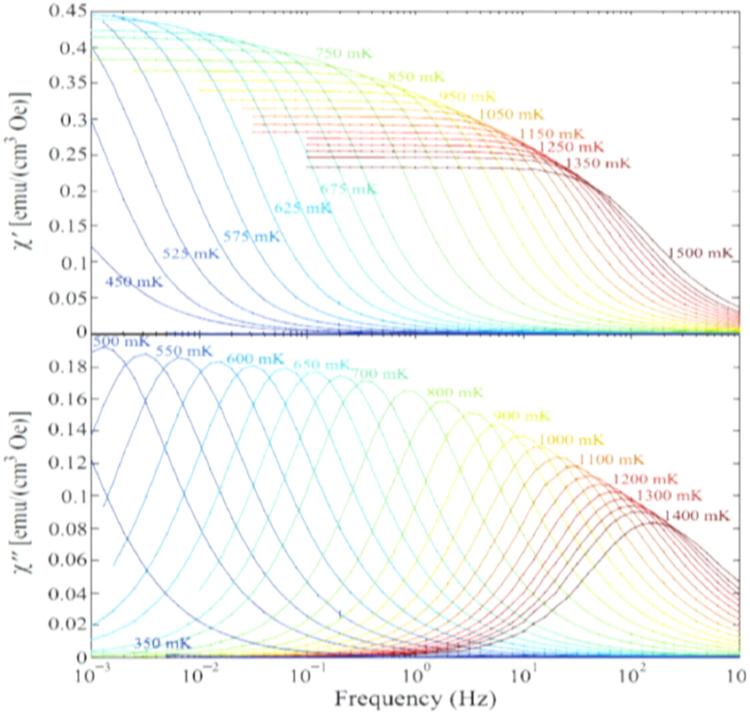

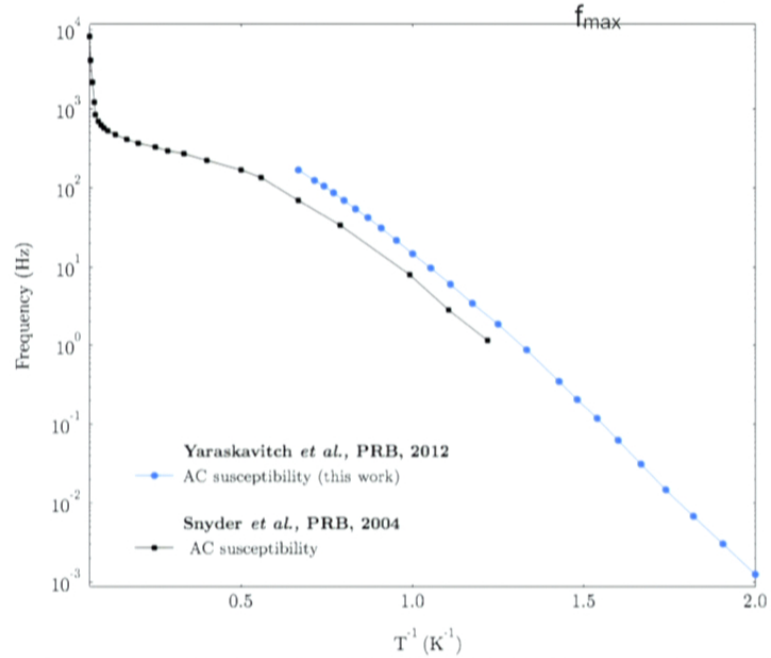

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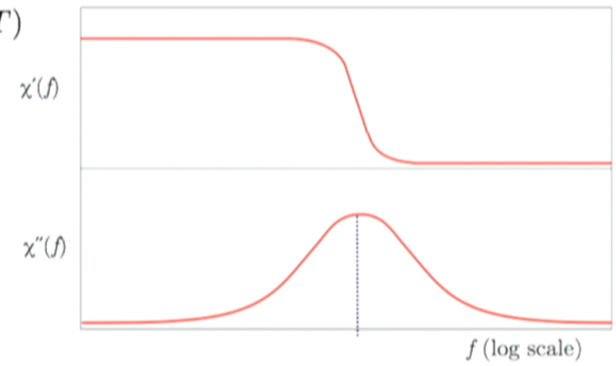

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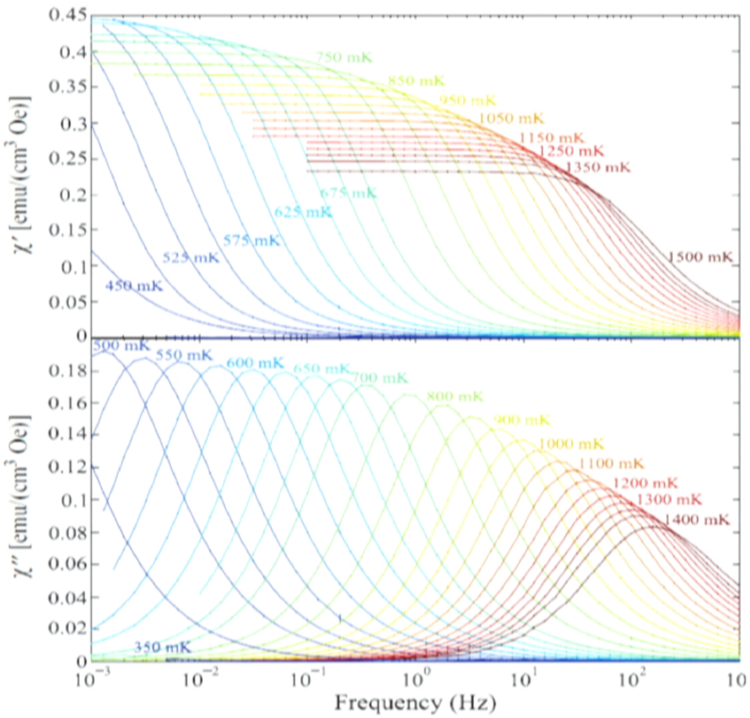
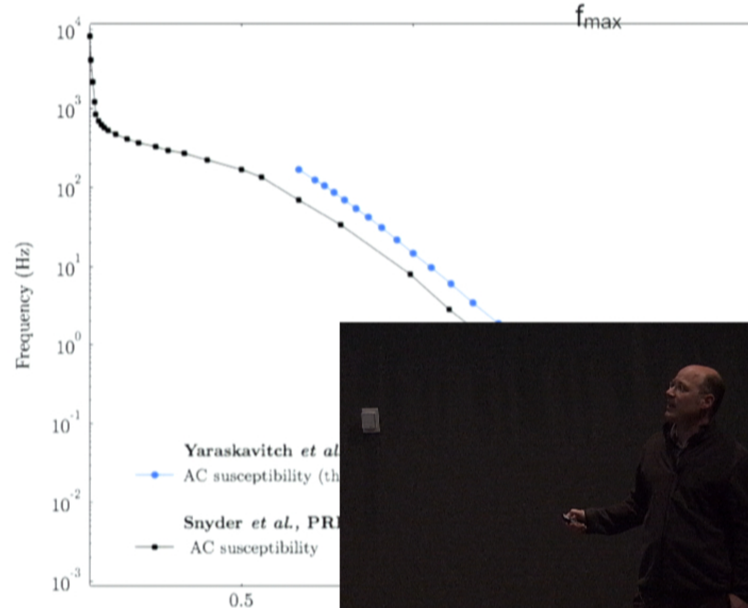
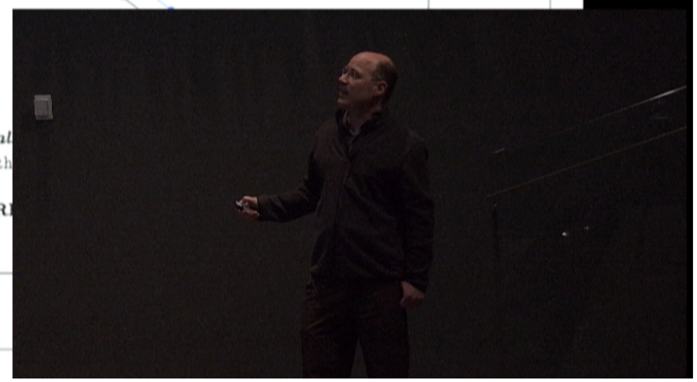
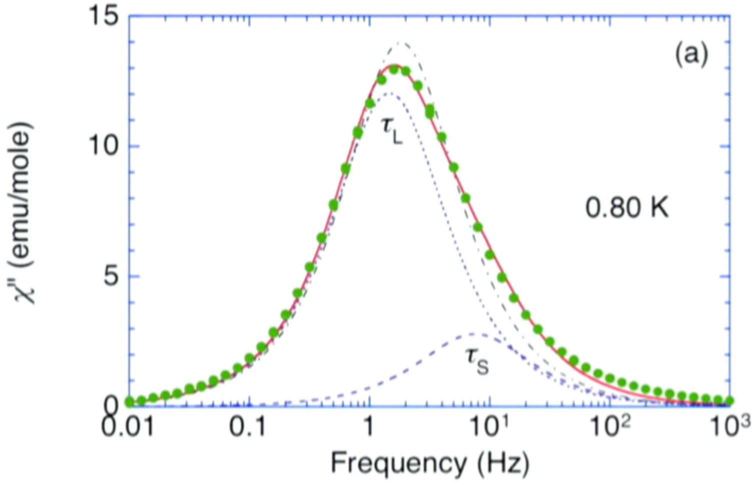


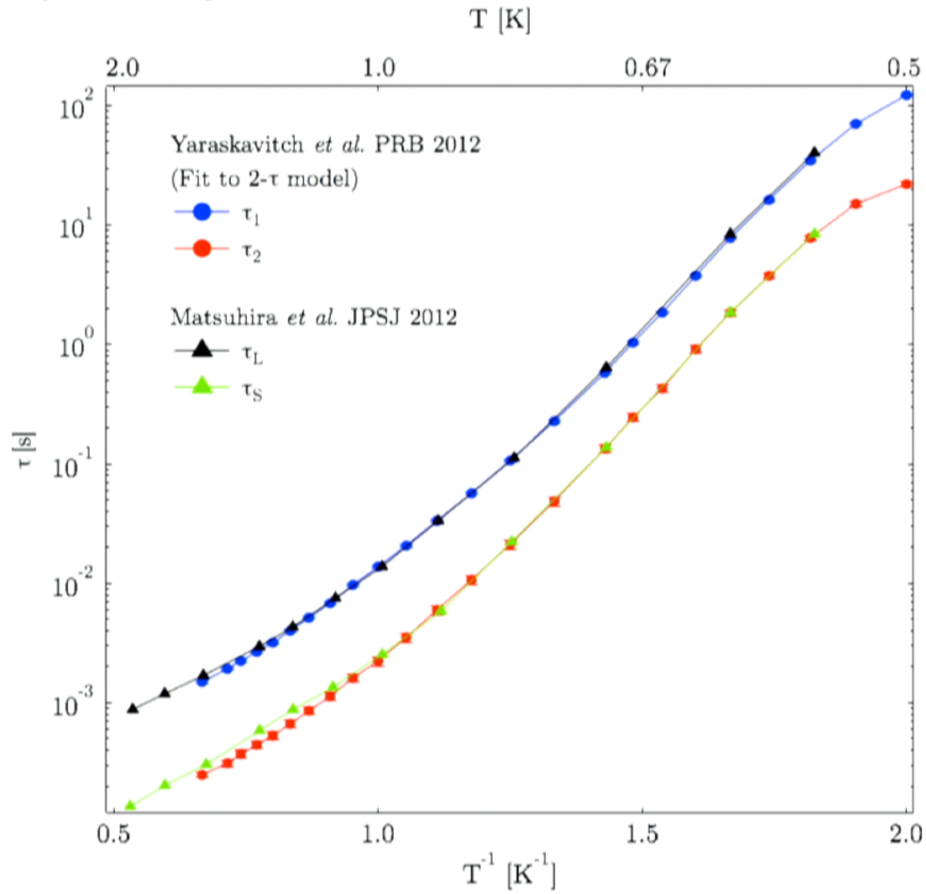




Comparison of our ac susceptibility measurements with Matsuhira *et al*

- The ac susceptibility was analyzed with a 2-τ Debye model to compare with the data from Matsuhira *et al.*
- The results agree very well



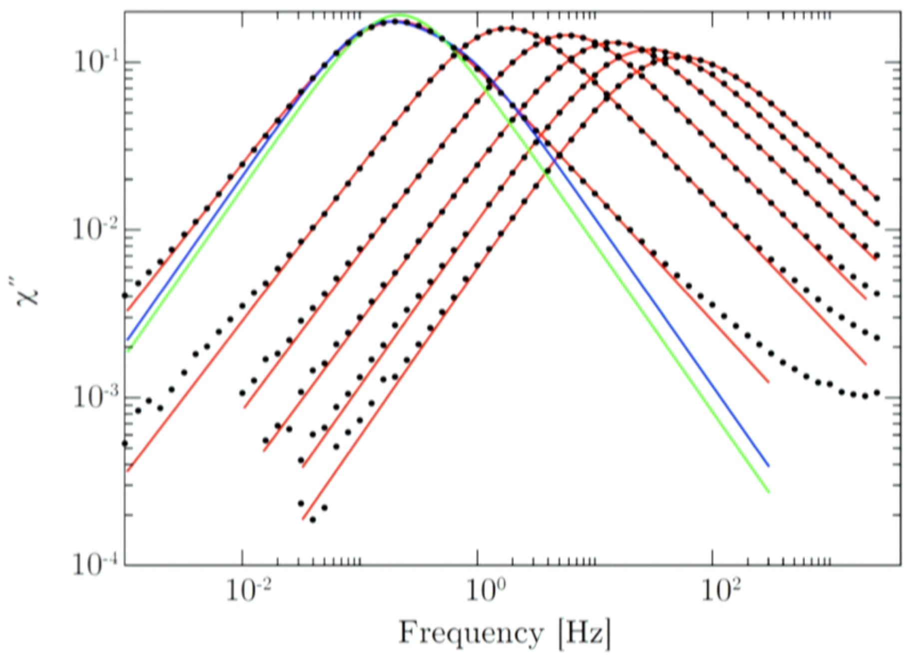


Matsuhira et al., JPSJ, 2011, Yaraskavitch et al. PRB, 2012

Transforming ac susceptibility and comparison to Debye, double Debye

$$\chi''(\omega) = \frac{1}{[(\tau\omega)^{\alpha_1 n}) + (\tau\omega)^{-\alpha_2 n}]^{1/n}} \quad (1)$$

$$C(t) = \langle M(0)M(t)\rangle = 2kT\int_{-\infty}^{\infty} \frac{\chi''(\omega)}{\omega}\cos(\omega t)d\omega$$



Black dots - ac susceptibility
Green - single Debye model
Blue - double Debye model
Red - fit to Eqn. (1)

Eqn. 1 from Biltmo and Henelius Nat. Comm. 2012

Questions:

1. What is determining the line shape?
2. Why is the time constant slower than expected at low T?

Conclusions of magnetization measurements

- It was demonstrated by two separate measurement techniques on two different magnetometers that the magnetic relaxation of $Dy_2Ti_2O_7$ for $0.475\ K < T < 1.1\ K$ is a stretched exponential with a long-time tail.

- By comparison to Monte Carlo simulation, it is suggested that:

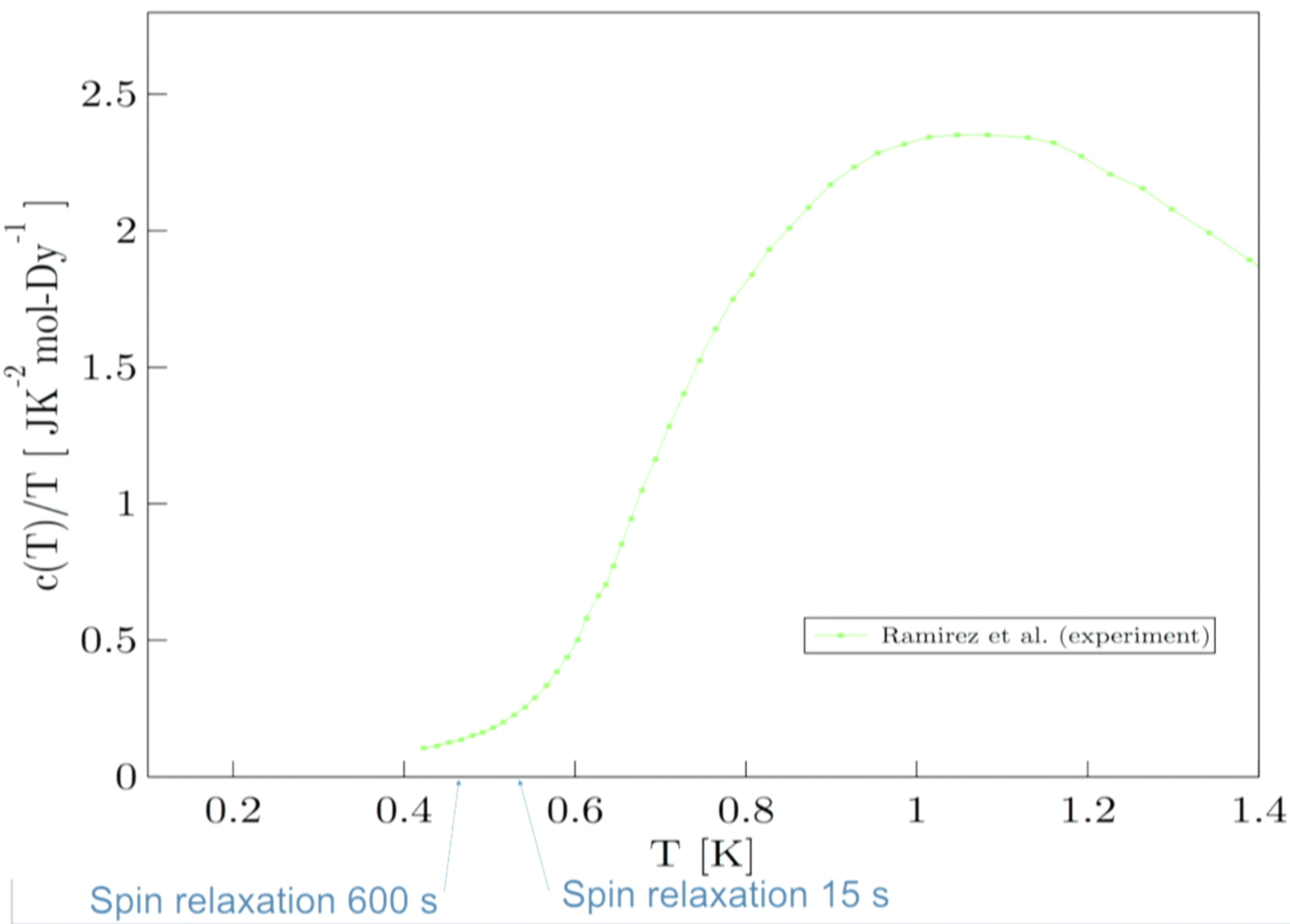
  surface effects are responsible for the stretching,

  a small amount (0.3%) of stuffed (extra Dy) spins are responsible for the long time tail.

- The 9 K energy barrier could be explained by an additional 4 K energy barrier due to a temperature dependent spin flip attempt rate proportional to the monopole density.

H. M. Revell, L. R. Yaraskavitch, J. D. Mason, K. A. Ross, H. M. L. Noad, H. A. Dabkowska, B. D. Gaulin, P. Henelius and J. B. Kycia, Nature Physics, **9** 34 (2013).

Previous specific heat measurements



Thermal equilibration time:

- Ramirez *et al.* ~15 s
- Klemke *et al.* ~ 600 s
- Others did not specify

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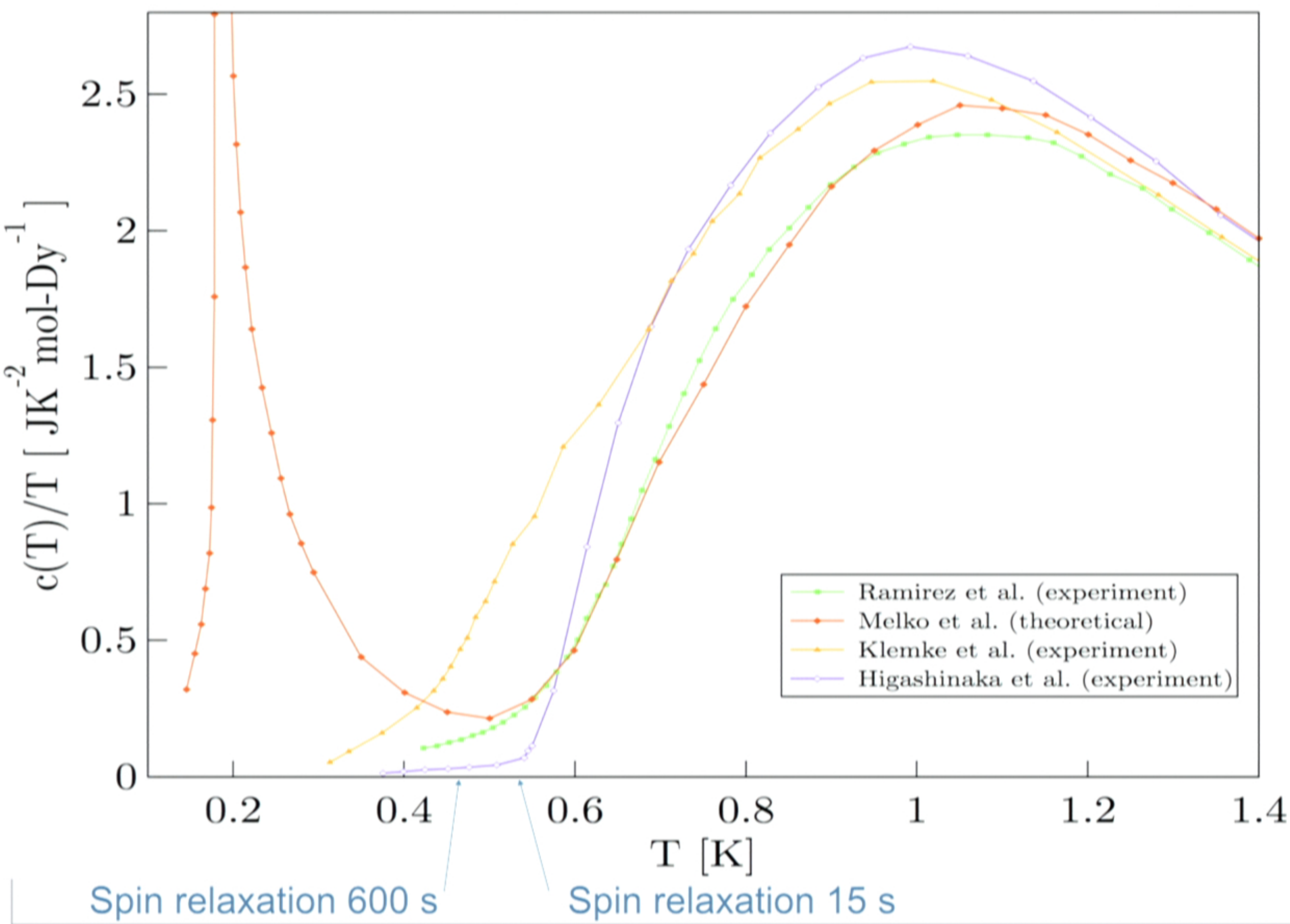

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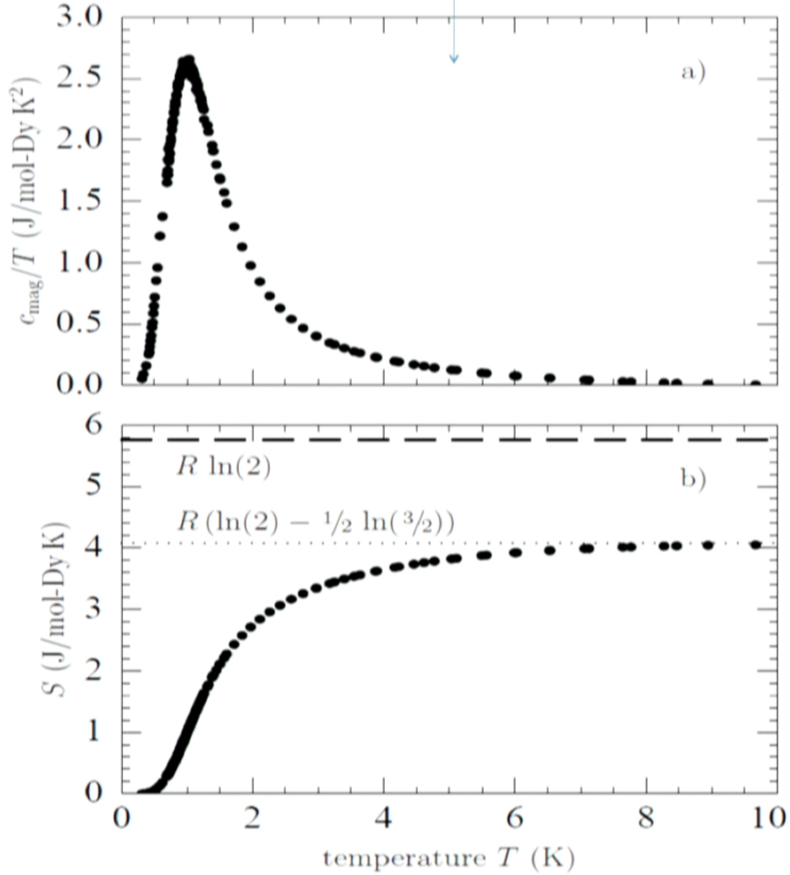
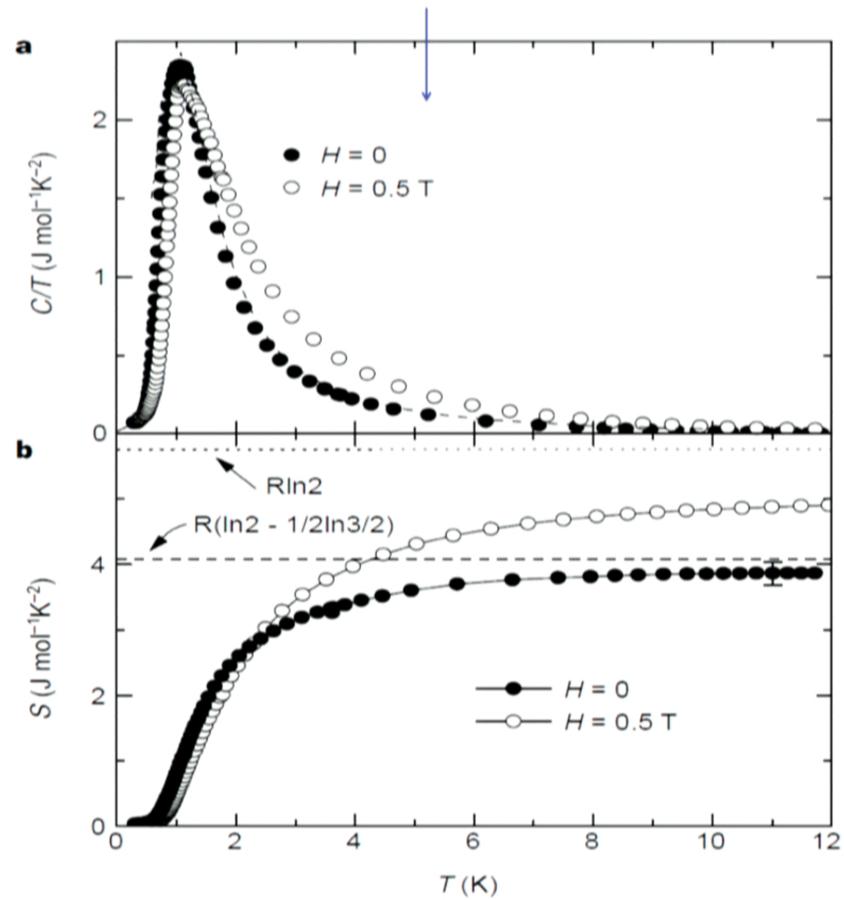
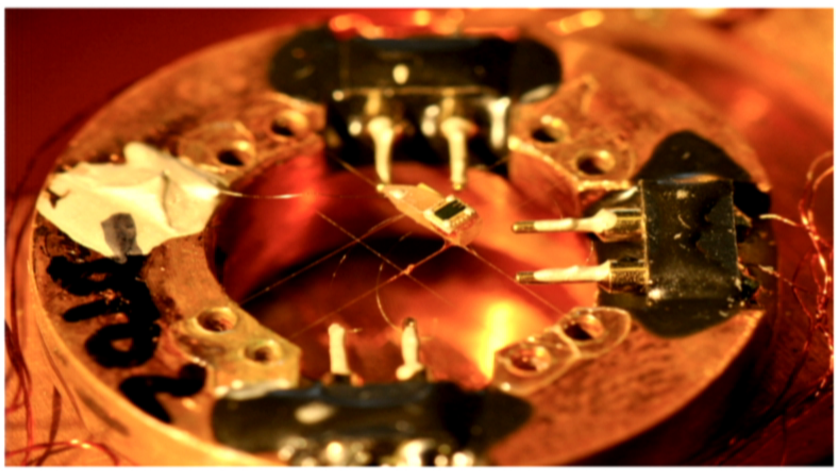
Entropy: Klemke *et al.* Ramirez *et al.*





Thermal relaxation calorimetry



Single crystal of $Dy_2Ti_2O_7$ in calorimeter

Heat flow rate across weak link of thermal conductance *K:*

$$\dot{Q} = K\Delta T$$

Ideal thermal relaxation time:

$$\tau = C \,/\, K$$

[H.Tsujii, B.Andraka, K.A.Muttalib, Y.Takano, Physica B 329–333 (2003) 1552–1553]

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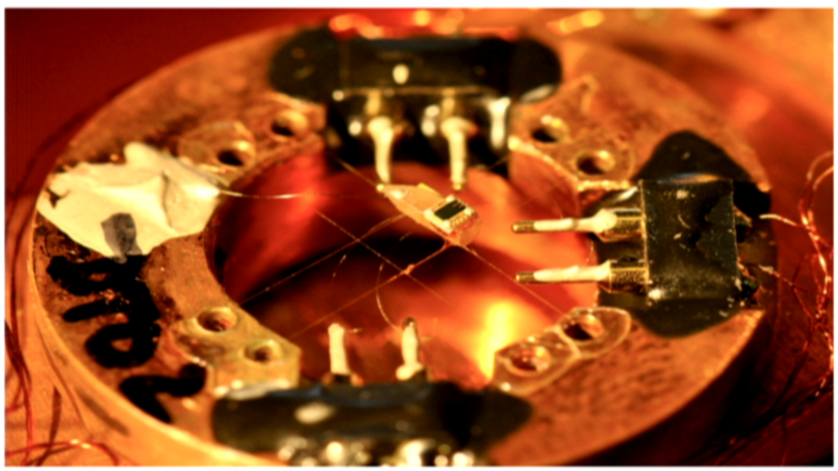

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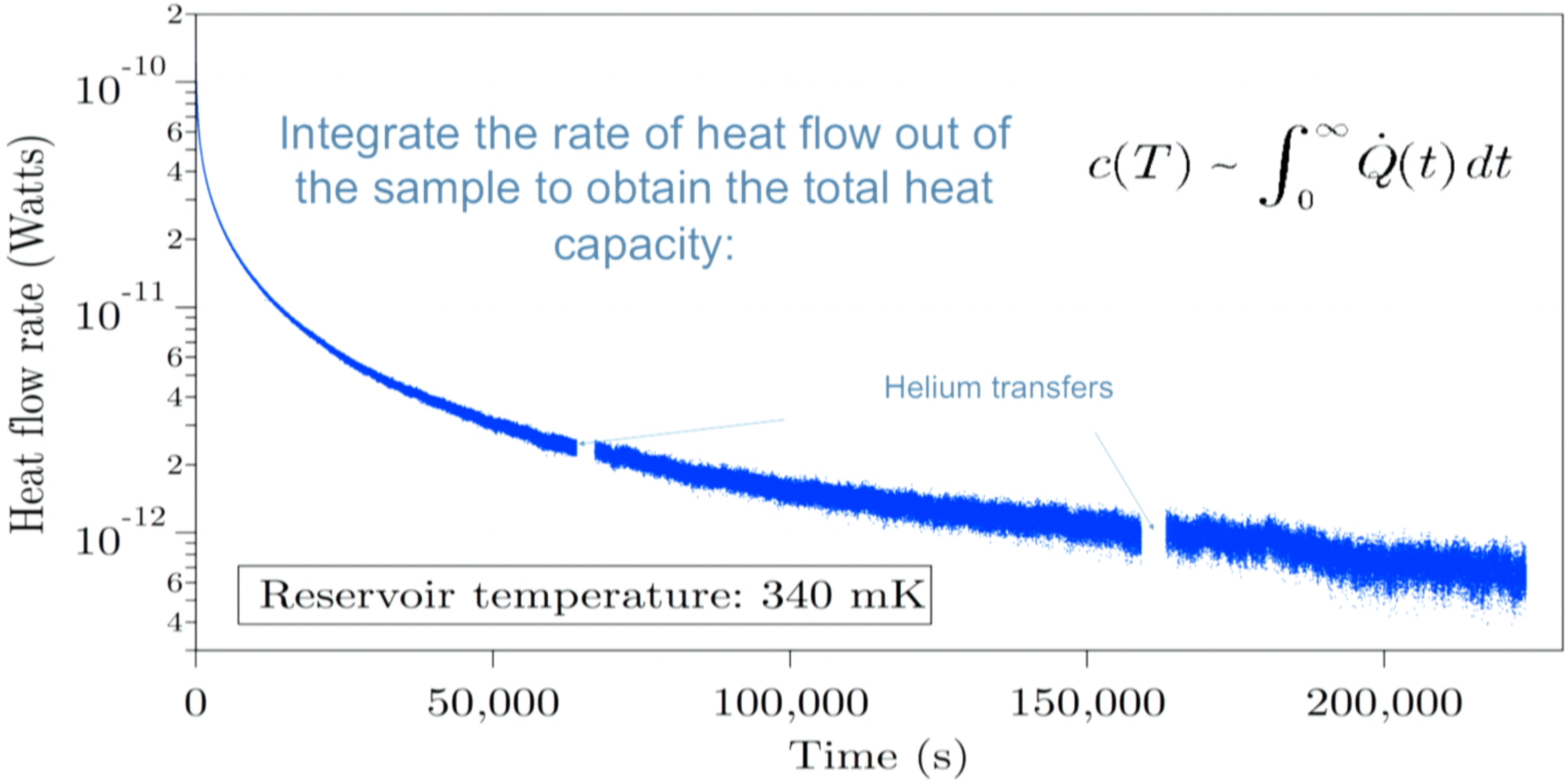
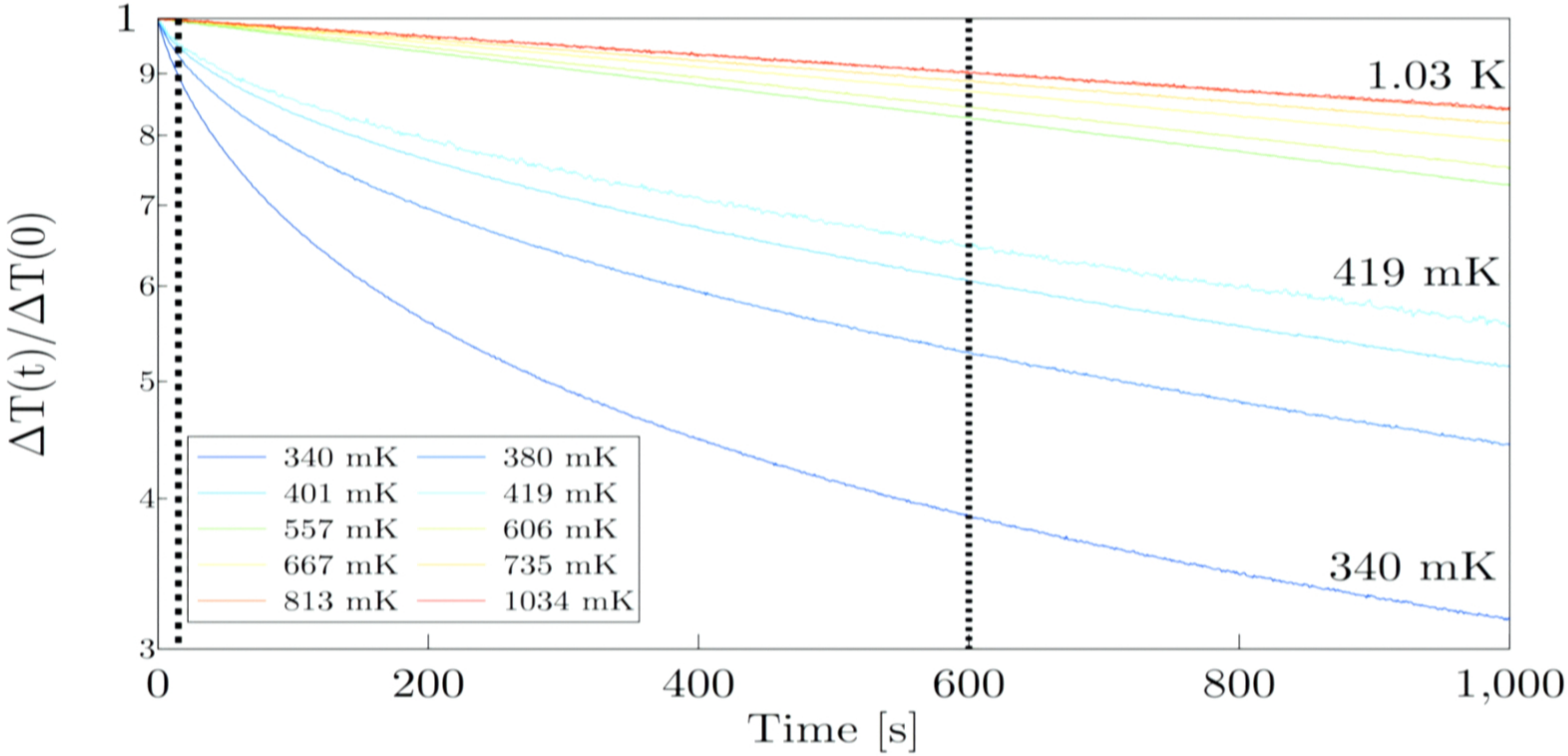
Thermal relaxation



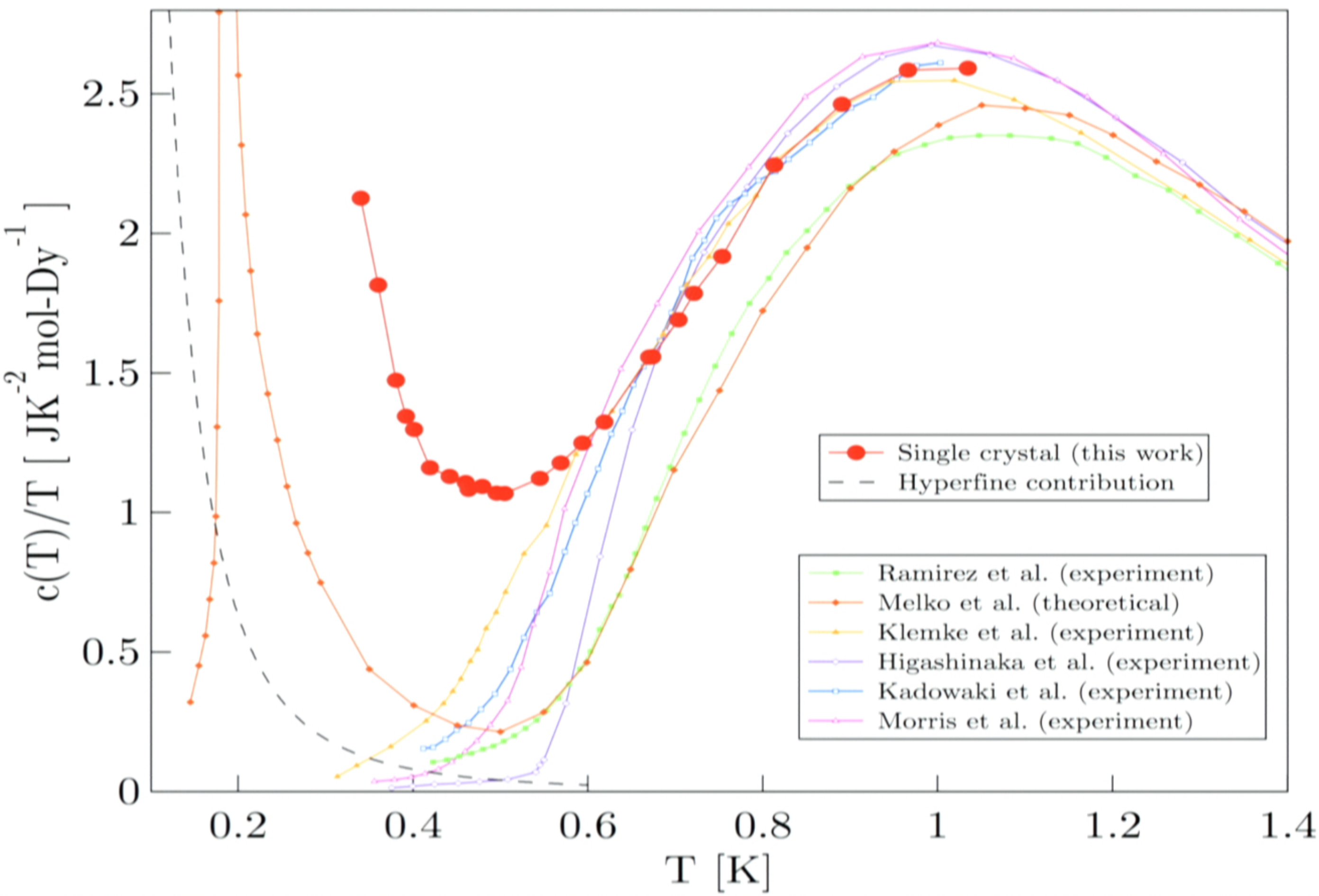
Thermal Relaxation in $Dy_2Ti_2O_7$

(data for single crystal)



Specific heat of $Dy_2Ti_2O_7$

(data for single crystal)



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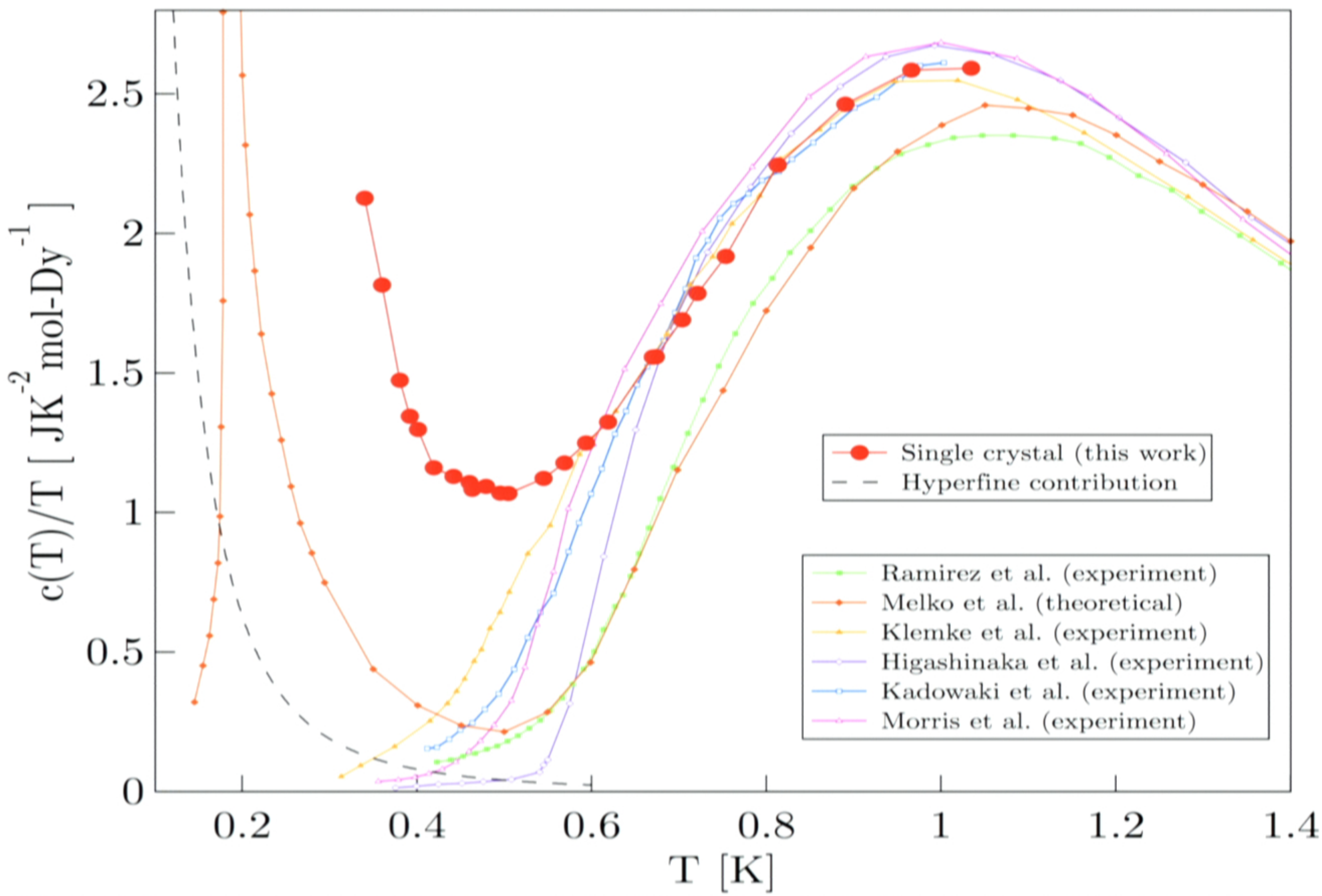
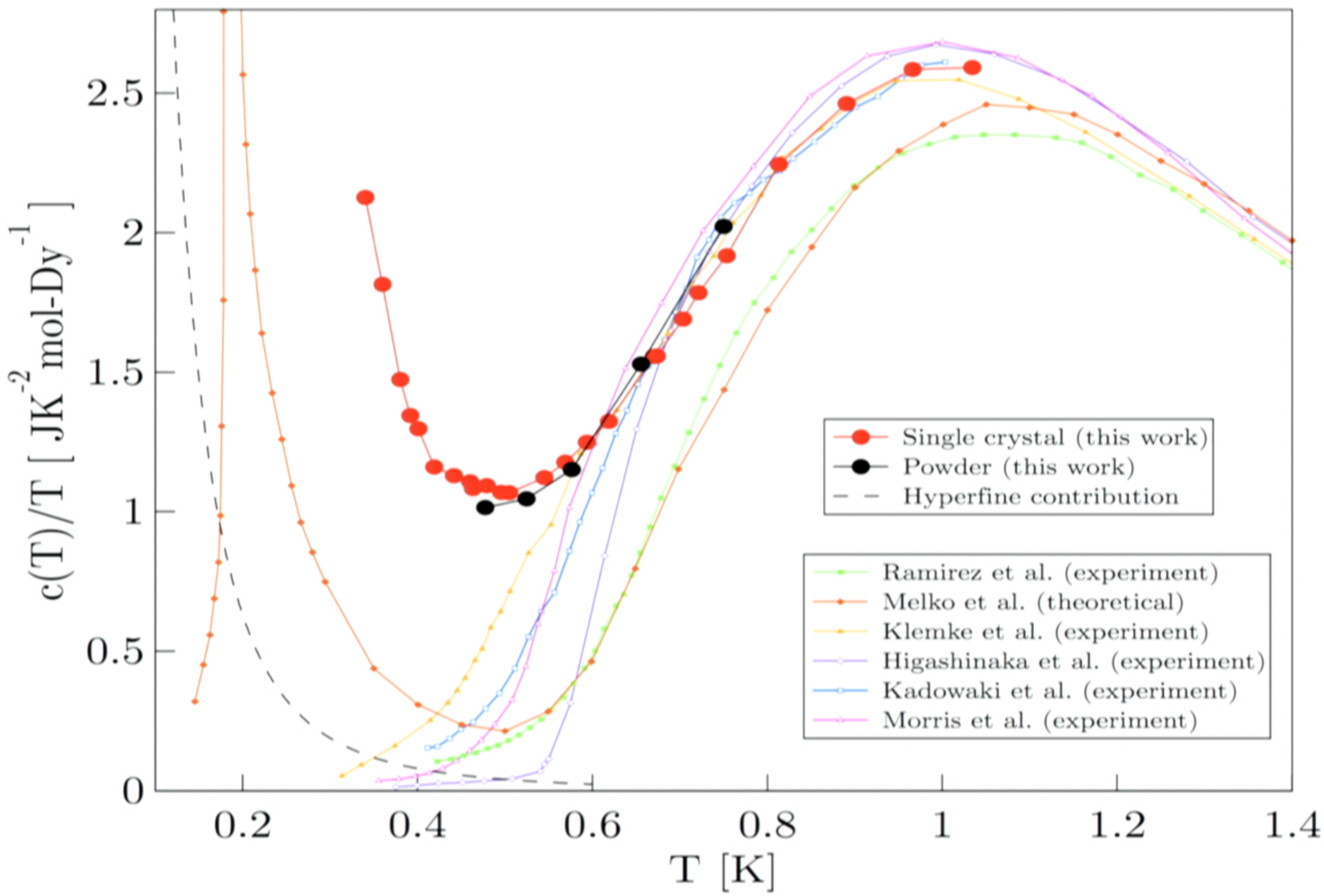
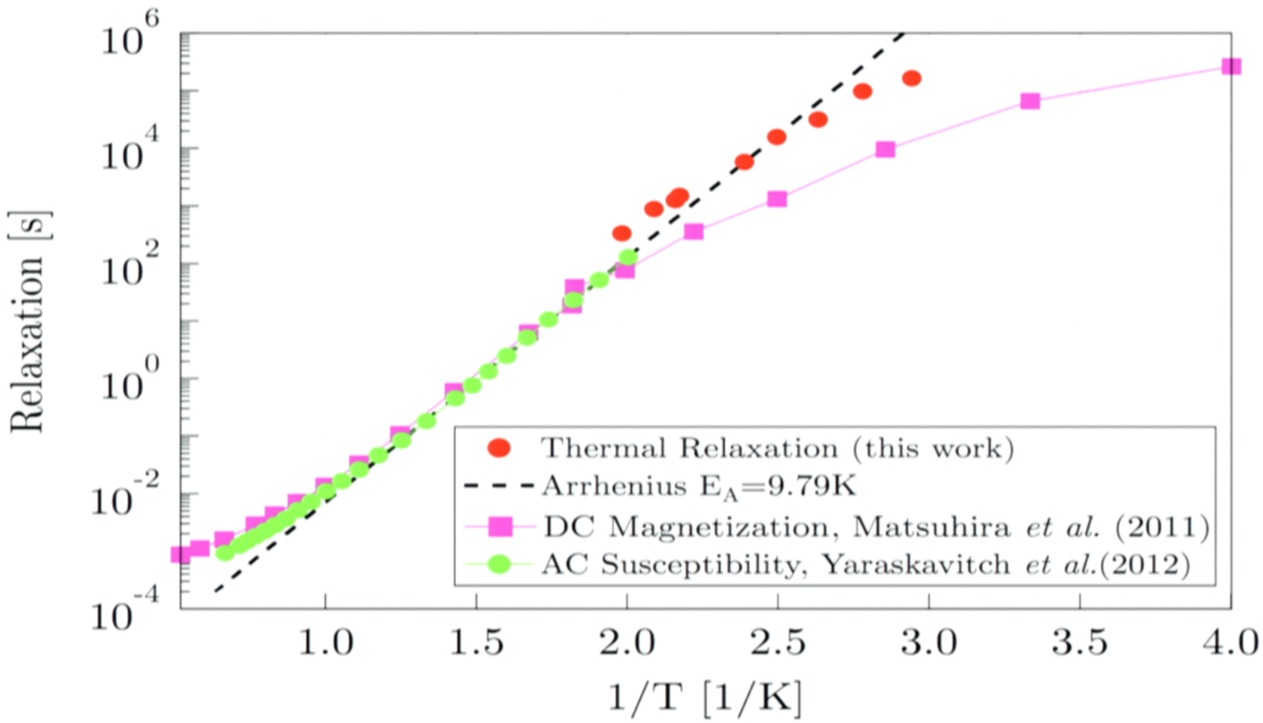


Specific heat of $Dy_2Ti_2O_7$

(Data for Powder Sample)



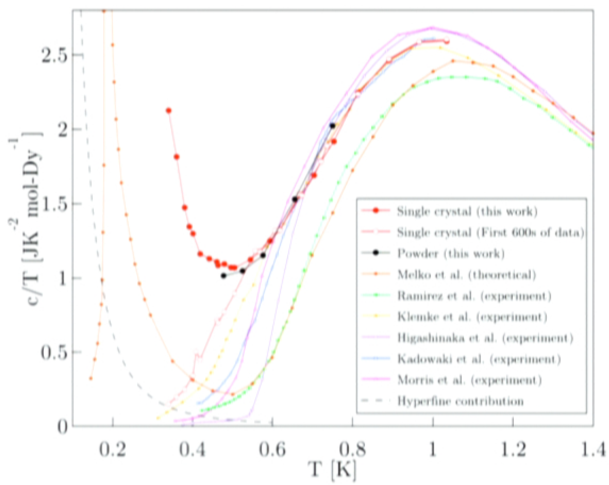
Low temperature equilibration time for $Dy_2Ti_2O_7$

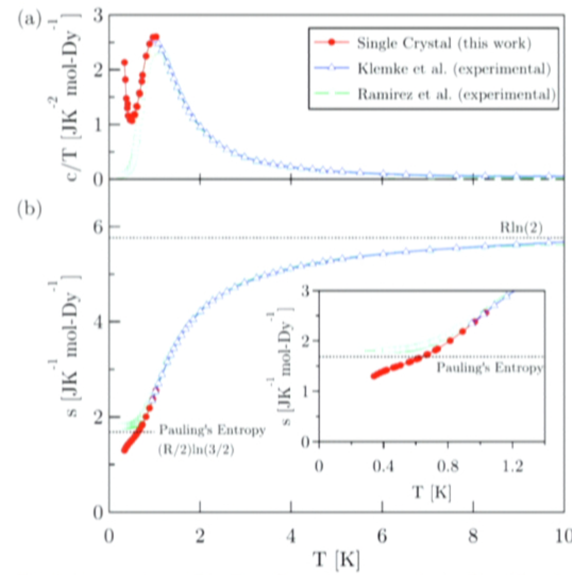


Other experiments (eg. neutron, muon-SR) should use these time constants as a guideline to ensure that they are investigating true equilibrium behaviour of this material

Summary of Specific Heat Result

- Upturn in c/T observed. Pauling residual entropy not seen when in equilibrium.
- Measured on a single crystal and a powder sample
- Different from Melko, den Hertog, Gingras prediction (Talk to Michel Gingras for recent results)
- c/T does not go to zero at 0.5K. Spin ice and ordering state coexist





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