Hellman Lab

LBL Instrumentation Colloquium

Specific Heat Measurements of Films and Tiny Crystals Using Si-micromachined Nano-calorimeters

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Magnetic and thermodynamic properties strongly affected by nanoscale structure

Structure may arise deliberately (multilayers, chemically synthesized nanoparticles), or from vapor deposition processes

Magnetic nanostructure central to modern applications, particularly magnetic recording

Thermodynamics: nanostructure may stabilize phases other than bulk equilibrium

Modern magnetometry is sensitive enough to study tiny volumes of material

Calorimetry traditionally has not been: *Si micromachined nanocalorimeters*

1. Device fabrication, principles of measurement, thermal characterization
2. Examples of samples measured (magnetic films)

Thanks to

Calorimeter development:

P. W. Rooney (PhD ‘95)
E. N. Abarra (PhD ‘96)
M. T. Messer (MS ‘93)
B. L. Zink (PhD ‘03)
S. Wohlert (PGR ‘99)
R. Sappey (PGR ‘00)
B. Revaz (PGR ‘01)
D. Queen (current PhD student)
D. W. Denlinger (MS ‘94)
K. Allen (PhD ‘98)
S. K. Watson (PGR ‘97)
D. K. Kim (PhD ‘01)
E. Janod (PGR ‘98)
D. Lieberman (PhD ‘01)
R. Pietri (PGR ‘04)
D. Cooke (current PhD student)

Samples and Measurements shown here:

B. Revaz, M.-C. Cyrille, I. K. Schuller (Fe/Cr multilayers)
B. Zink, E. Janod, P. Xiong, R. C. Dynes (a-Gd-Si)
E. N. Abarra, Y. J. Tang, J. Boerio-Goates, B. Woodfield, A. Navrotsky, K. Takano, A. Berkowitz (CoO)

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Small Sample Calorimetry

Problem for small samples:

1. Heater, thermometer, sample platform all have heat capacity (“addenda”) – swamps sample
   Solution: make addenda tiny (thin films)

2. Electrical leads to heater, thermometer thermally link sample to environment – not easy to make adiabatic measurement
   Solution: work in time domain and use semi-adiabatic methods
      (sample thermally isolated enough: $\tau_{int} < \tau_{ext}$)
      ac method, relaxation method, pulses, etc.

Sample platform: making the addenda small

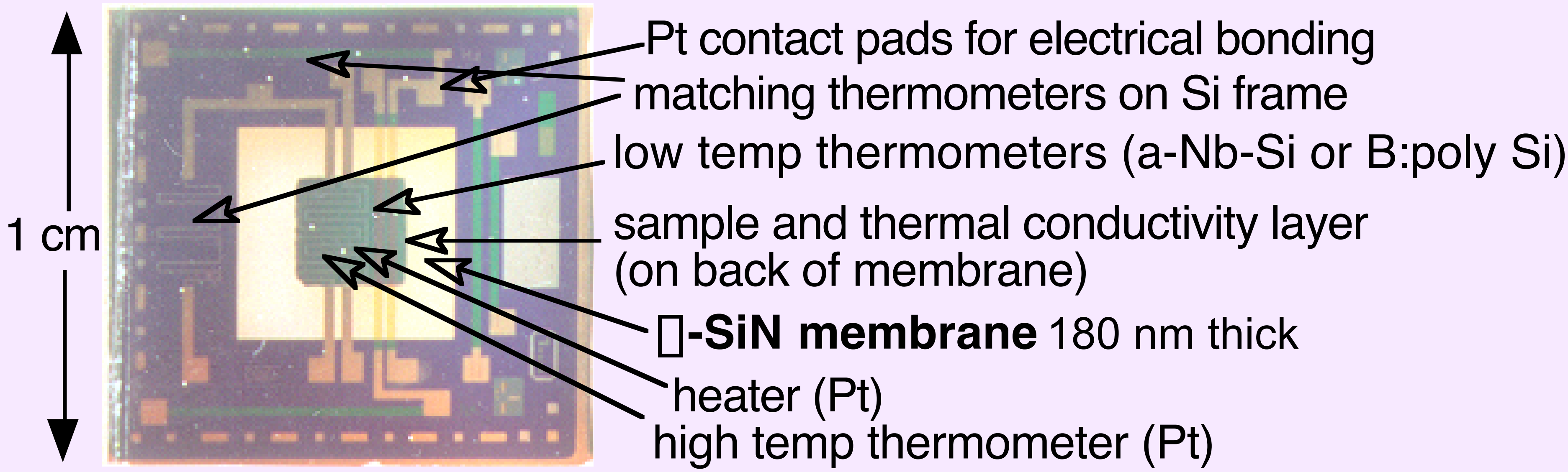
For small addenda, straightforward to use thin film thermometers and heaters, but substrate/sample platform is a problem

Examples of approaches (for C_p measurements of films):

1. Use high Debye temp substrates such as Al_2O_3. Good for temperatures < approximately 40K.

2. For a wide temperature range, use a very thin substrate/ membrane of some material: Si, Kapton polyimide, GaAs, low stress *a*-Si-N ** (*a*-Si-N also has a high Debye temp).

Micro/nanocalorimetry: overview



Heat capacity:

- μg and sub-μg (films ~100 nm thick)
- Evaporated/sputtered films; powders; tiny crystals;
- 1-500K (soon to 0.3K and 800K)
- 1-8T (working on 45T, 100T pulsed)

Thermal conductivity

Thermopower

D. W. Denlinger, E. N. Abarra, Kimberly Allen, P. W. Rooney, S. K. Watson, and F. Hellman , "Thin film microcalorimeter for heat capacity measurements from 1.5 K to 800 K", *RSI* **65**, 946 (1994).

Microcalorimeter Construction

UC Berkeley Microfabrication Lab

4” DSP <100> Si Wafer

Microcalorimeter Construction

a-SiO_x electrical isolation layer
(1.5 μm LTO or 5000-6000 Å Thermal Oxide)

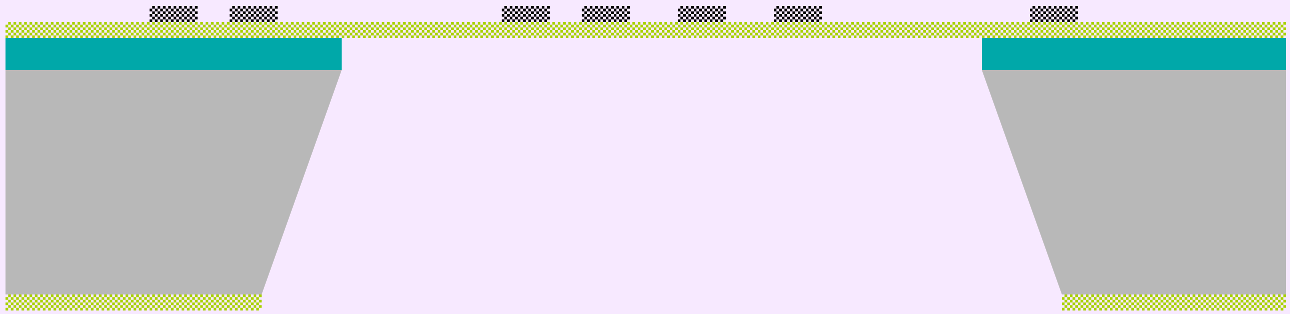
Microcalorimeter Construction

1800-2000 Å low-stress *a*-SiN_x
(LPCVD @ 835°C)

Microcalorimeter Construction

Pt Leads, High T Thermometers, Heater
a-Nb-Si Low T Thermometers

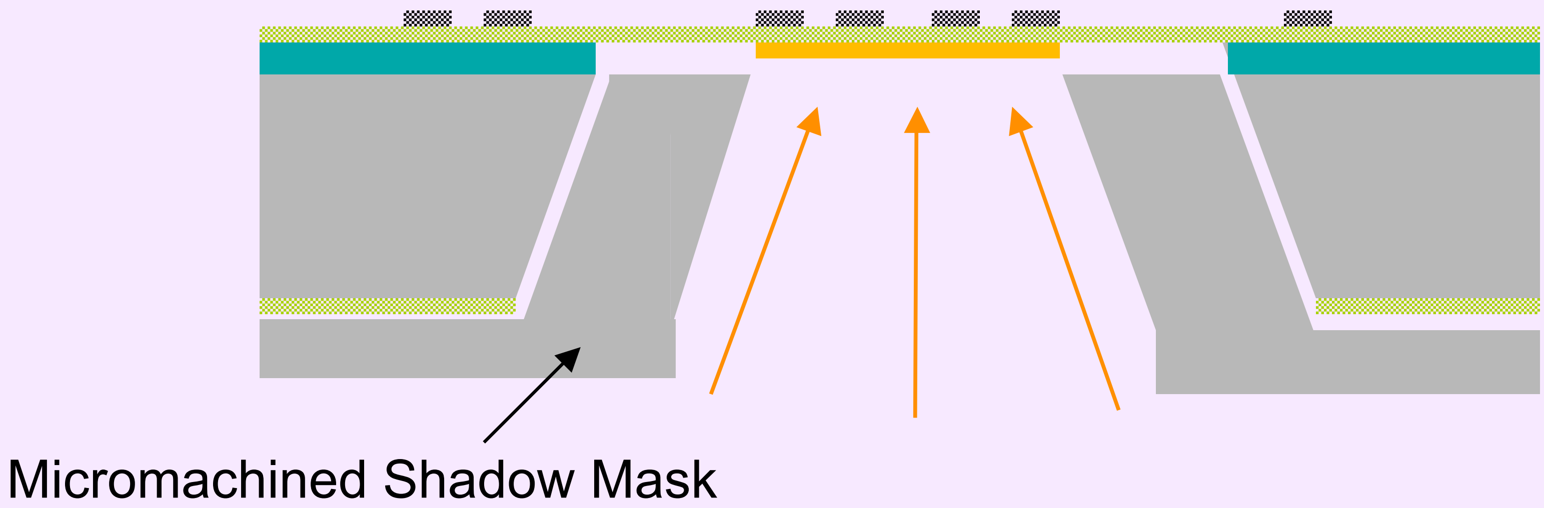
Microcalorimeter Construction



Form Membrane (1800 Å thickness, 0.5cm x 0.5cm) with KOH anisotropic wet Si etch

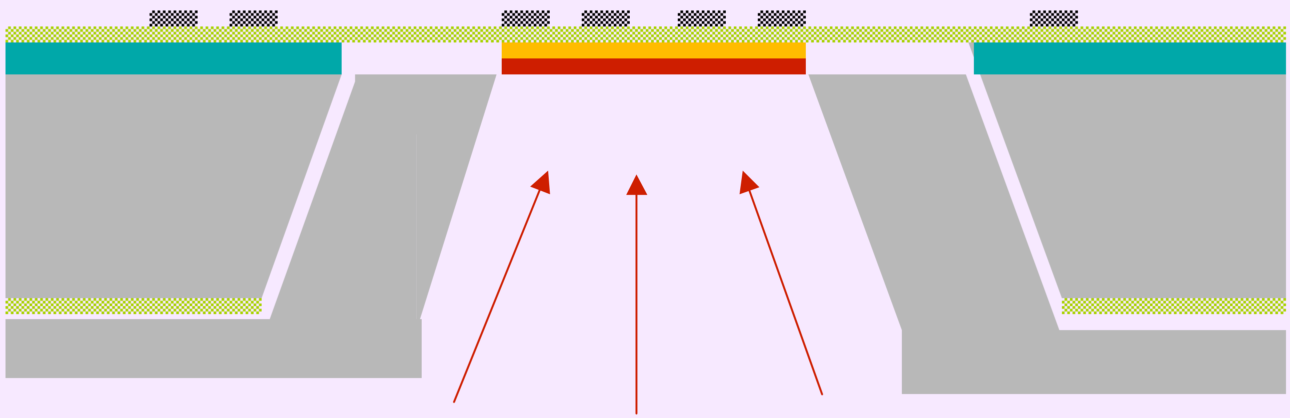
Thermal Conduction Layer

Deposit Thermal Conduction layer
~2000 Å of Al, Cu, Au, Ag



Sample: Heat Capacity, Vapor Deposited Films

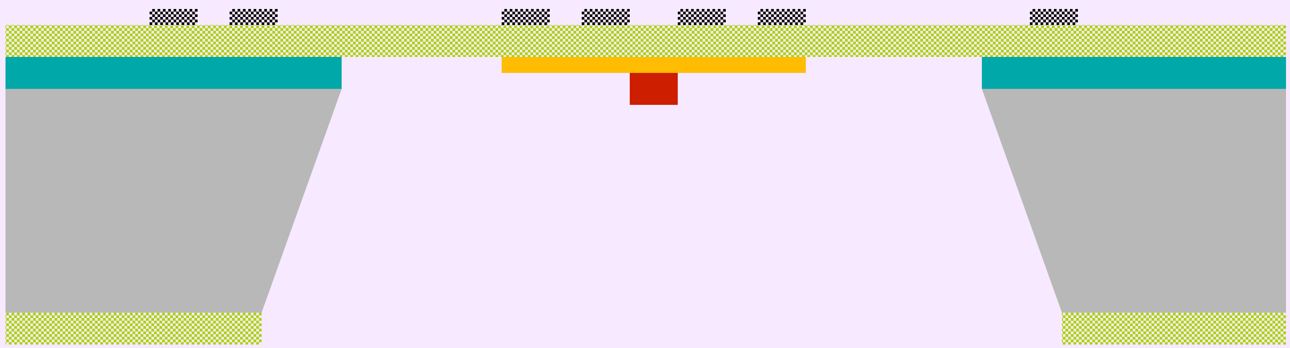
~2000 Å vapor deposited sample (~1 g)



Deposit sample only on conduction layer

Or bulk crystals

~200 μg attached with Indium or grease
(measure In/grease separately)
Use thicker membrane devices



Measuring Specific Heat: Small ΔT Relaxation Method

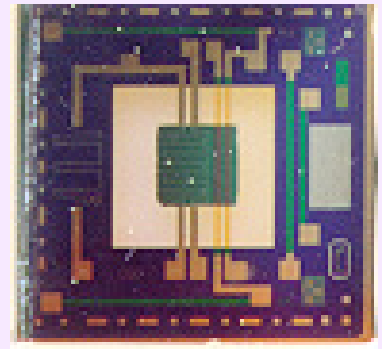
Small ΔT Relaxation Method:

1) Power P into sample heater
2) Measure ΔT in steady state

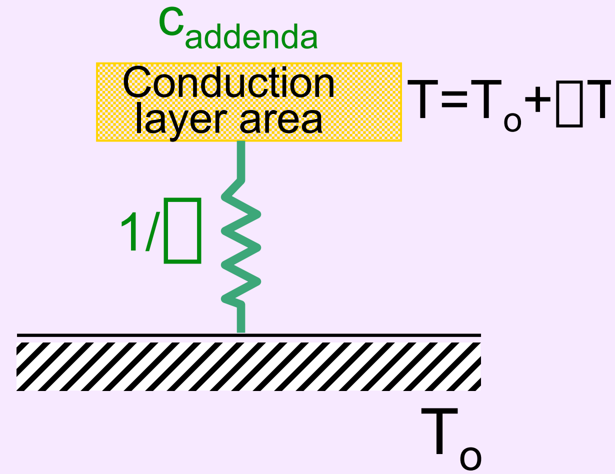
   $\kappa = P/\Delta T$

3) Time t=0, turn off heater:

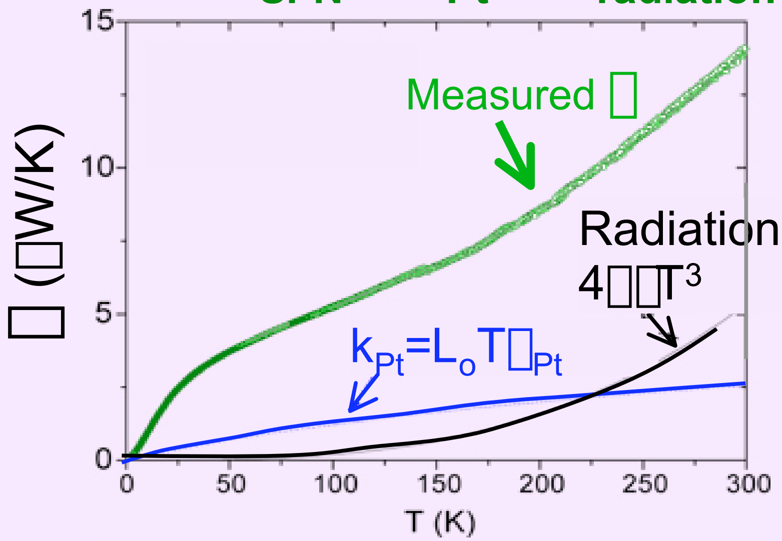
   $\Delta T\, e^{(-t/\tau)}$



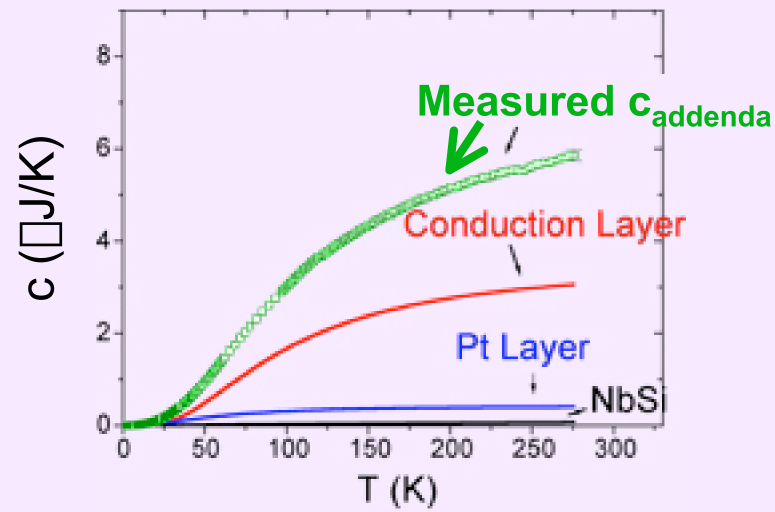
$$c_{addenda} = \kappa\,\tau$$



$\kappa = \kappa_{Si\text{-}N} + \kappa_{Pt} + \kappa_{radiation}$



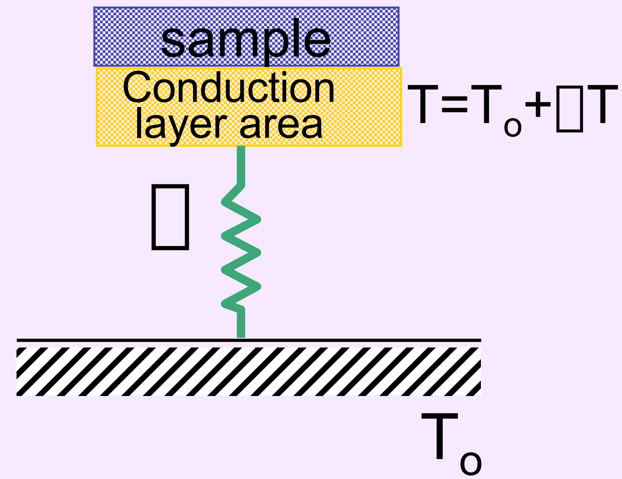
$c_{addenda} = c_{Si\text{-}N} + c_{cond} + c_{Pt} + c_{NbSi}$



Measuring Sample Specific Heat: repeat measurement with sample

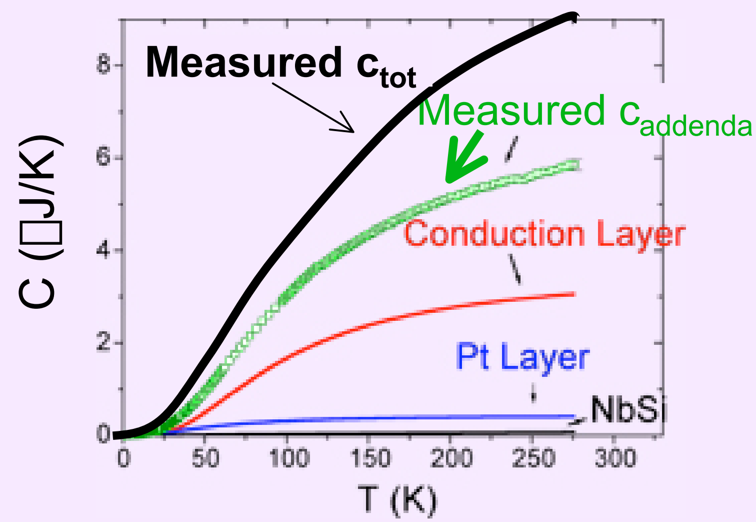
Small □T Relaxation Method:

1) Heat Q into sample heater
2) Steady state: □=Q/□T
   (measure, but unchanged)
3) Time t=0, turn off heater:
   □T $e^{(-t/□)}$

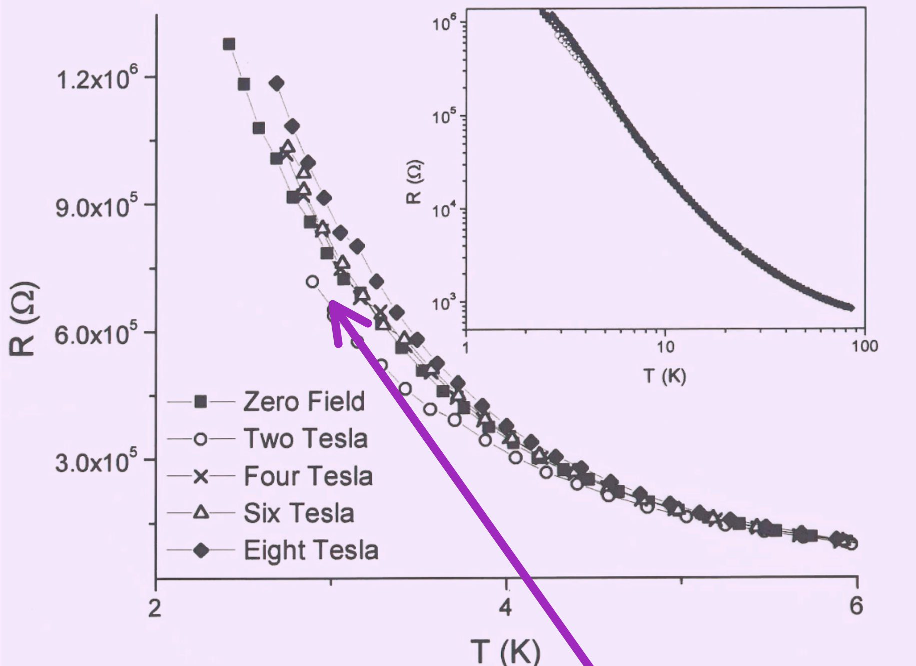


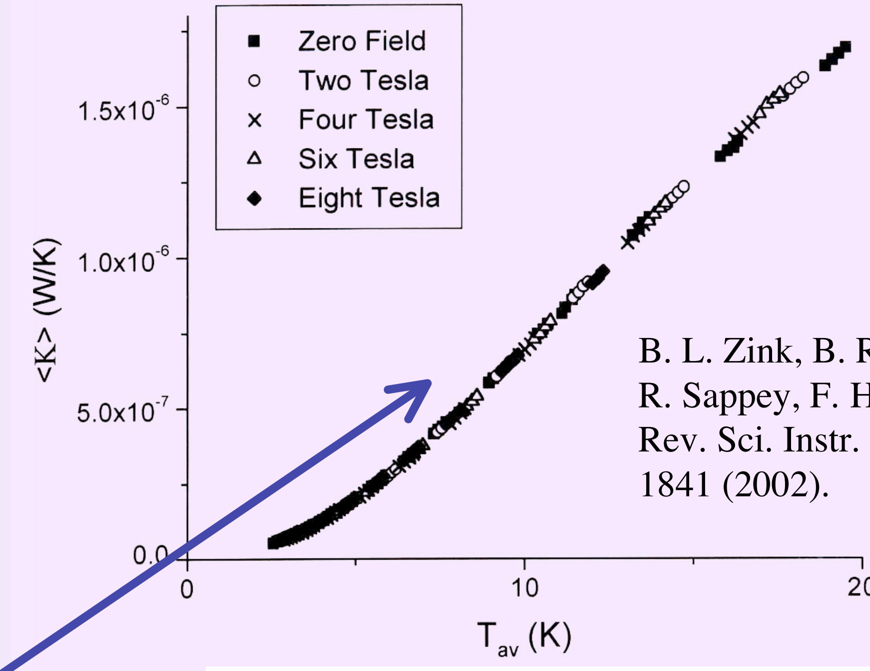
c_{total} = □ □

$c_{sample} = c_{tot} - c_{addenda}$



Calorimetry in Magnetic Field





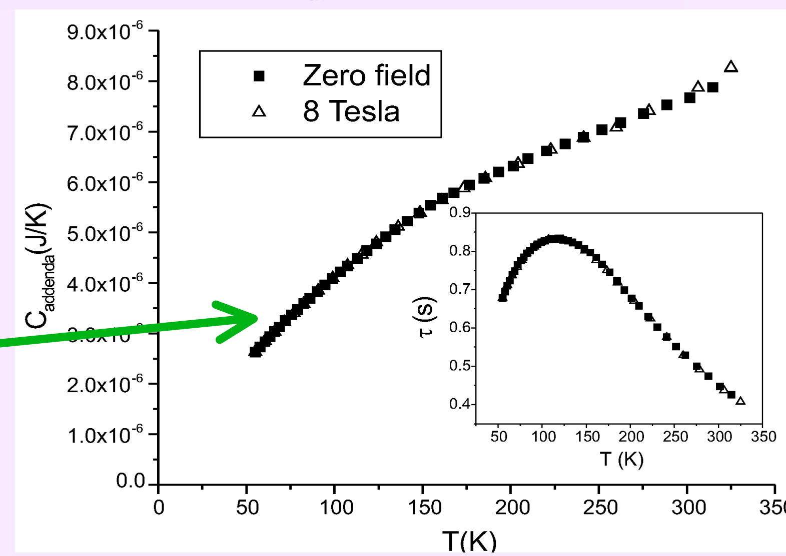
B. L. Zink, B. Revaz, R. Sappey, F. Hellman, Rev. Sci. Instr. **73**, 1841 (2002).

Device thermometers show magnetoresistance R(H)

Thermal link □ does *not*

Addenda heat capacity and □ do *not*

Measure □ in zero field; □(H) for addenda plus sample gives C(H) for sample

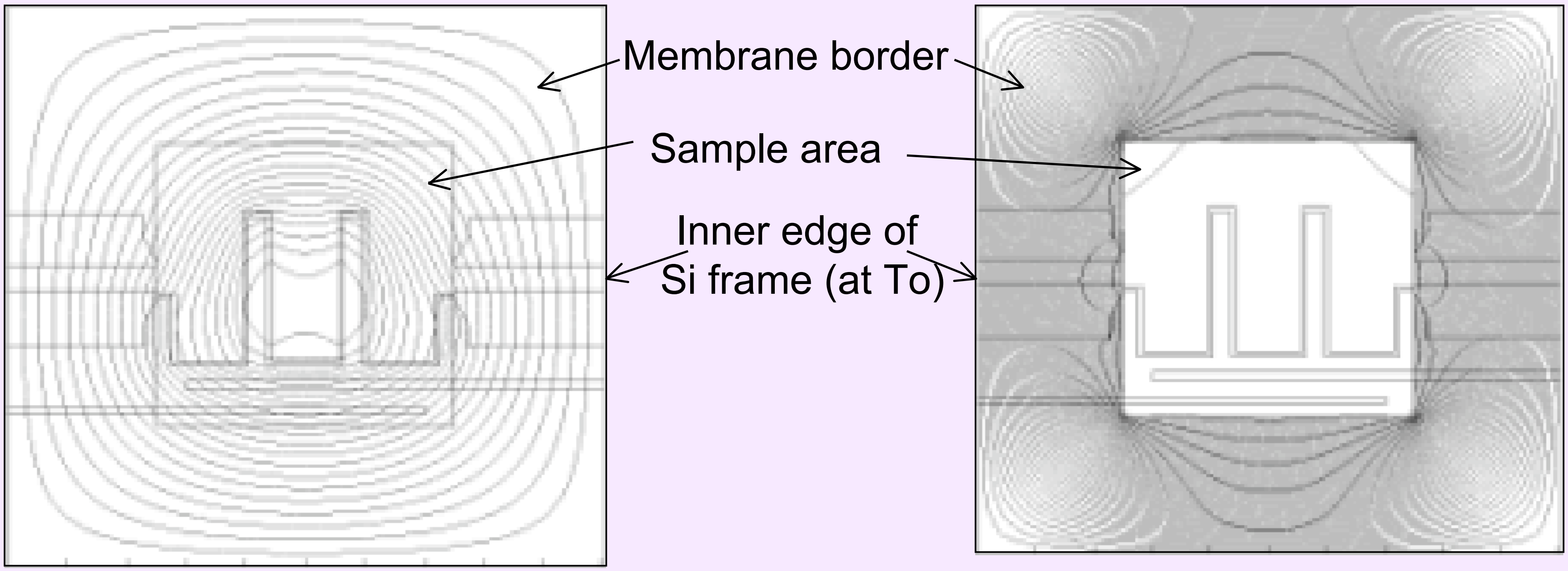


Numerical 2D simulations of heat flow: steady state (∂T/∂t = 0)

$$\cancel{c_{2D}(x,y)\frac{\partial T(x,y,t)}{\partial t}} - \left[\frac{\partial}{\partial x}\left(k_{2D}(x,y)\frac{\partial T(x,y,t)}{\partial x}\right) + \frac{\partial}{\partial y}\left(k_{2D}(x,y)\frac{\partial T(x,y,t)}{\partial y}\right)\right] = P_{2D}(x,y,t)$$

Empty membrane (no conduction layer): $k_{cond}/k_{mem} = 0$ (5% contours)

With Cu conduction layer: $k_{cond}/k_{mem} \sim 100$ (2% contours)



Numerical 2D simulations of heat flow: time dependence (P = 0)

$$c_{2D}(x,y)\frac{\partial T(x,y,t)}{\partial t} = \frac{\partial}{\partial x}\left(k_{2D}(x,y)\frac{\partial T(x,y,t)}{\partial x}\right) + \frac{\partial}{\partial y}\left(k_{2D}(x,y)\frac{\partial T(x,y,t)}{\partial y}\right) = P_{2D}(x,y,t)$$

Fit time dependence to single exponential with □; c= □□

Differential measurement method: $c_s = c_{tot} - c_{addenda}$

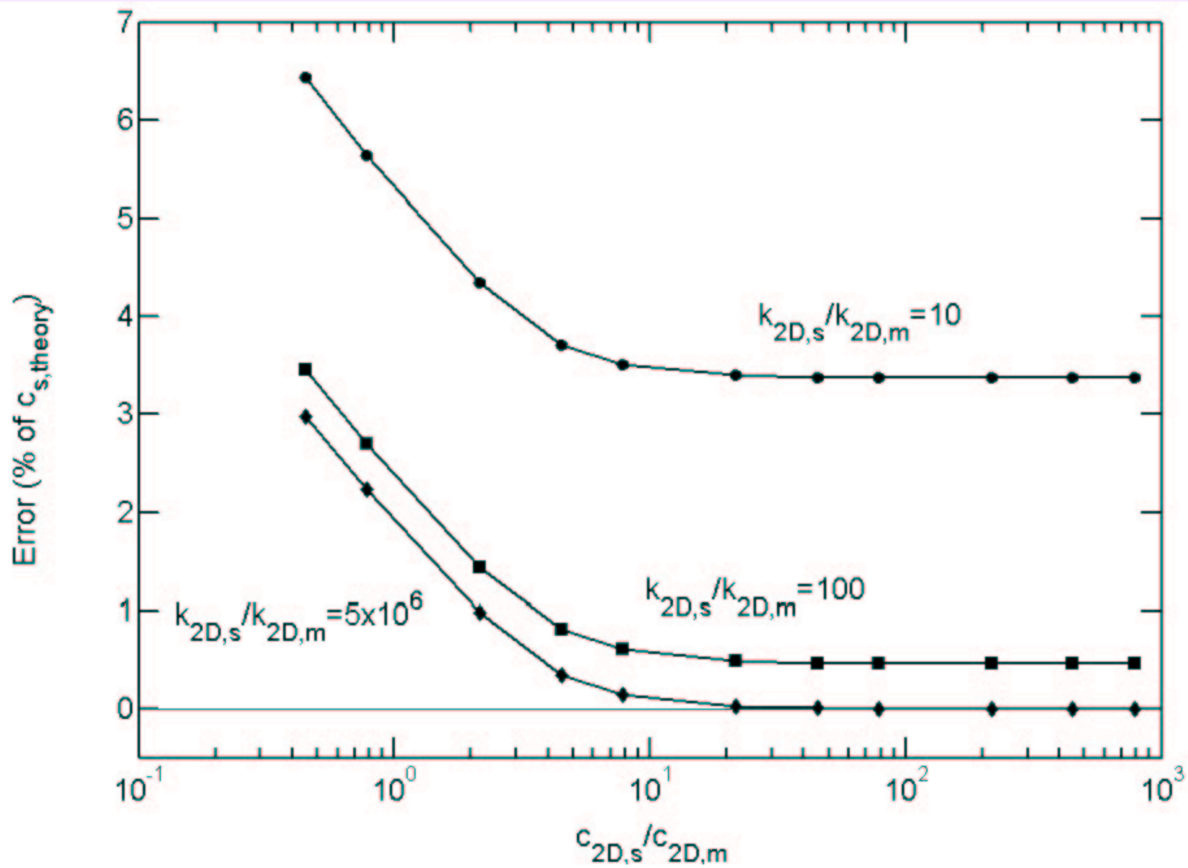
Simulate this with two layers of different thickness and take difference

<u>Results</u>:

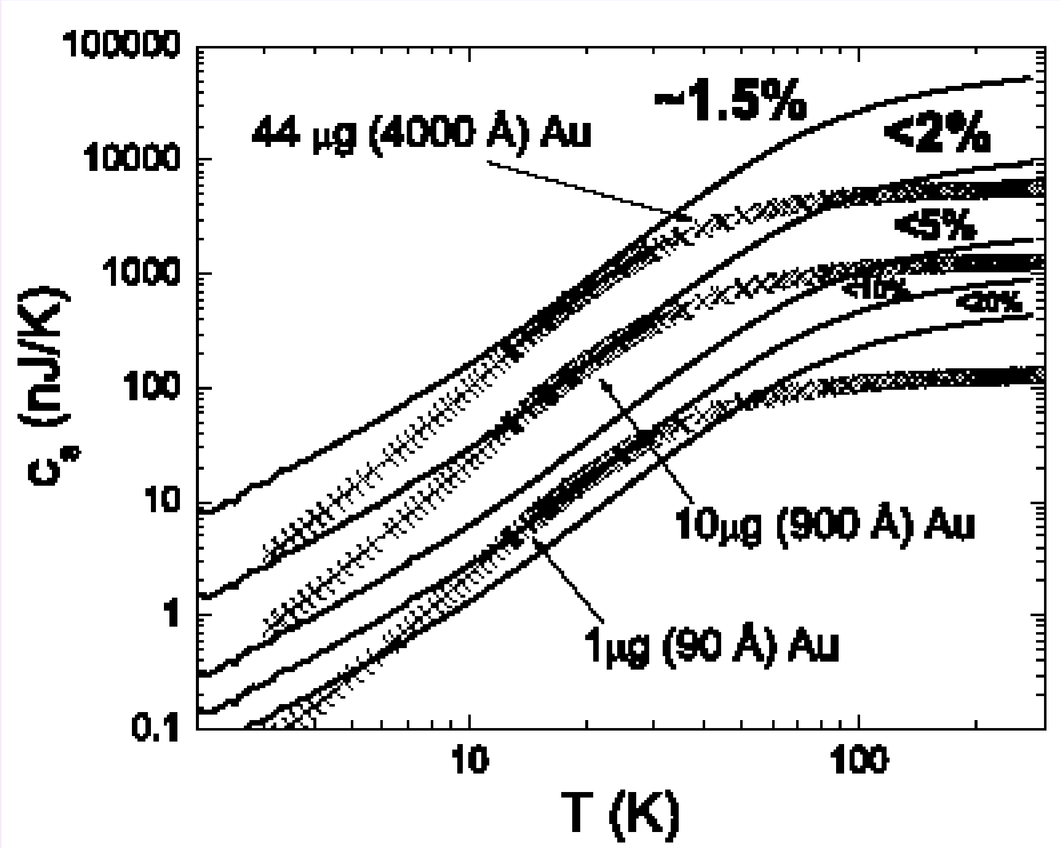
Relaxation method is exact for infinite k_{cond}/k_{mem}, c_{cond}/c_{mem}

Systematic error increases as these decrease

<1.5% in our limit (conduction layer~membrane thickness)



Error bars on sample specific heat Depends on sample "size" and T



Plot shows error bars for standard 180 nm membrane

Thicker membranes (1.5 μm) means attached samples need to be ~8x larger for same accuracy: (~400 μg) (*assuming good sample internal thermal conductivity*)

Use nanocalorimetry devices when other techniques won't work

- Material available only as vapor deposited films
  Multilayers, amorphous alloys, metastable materials
- Tiny crystals (e.g. from diamond anvil cell)
- Limited measurement space, e.g. small bore of high magnetic field, *in situ* in TEM or deposition system
- Self-contained measurement or "Lab on a chip" ideas
- Rapid heating and cooling
- Time resolved measurements (short internal □)

Examples of measurements

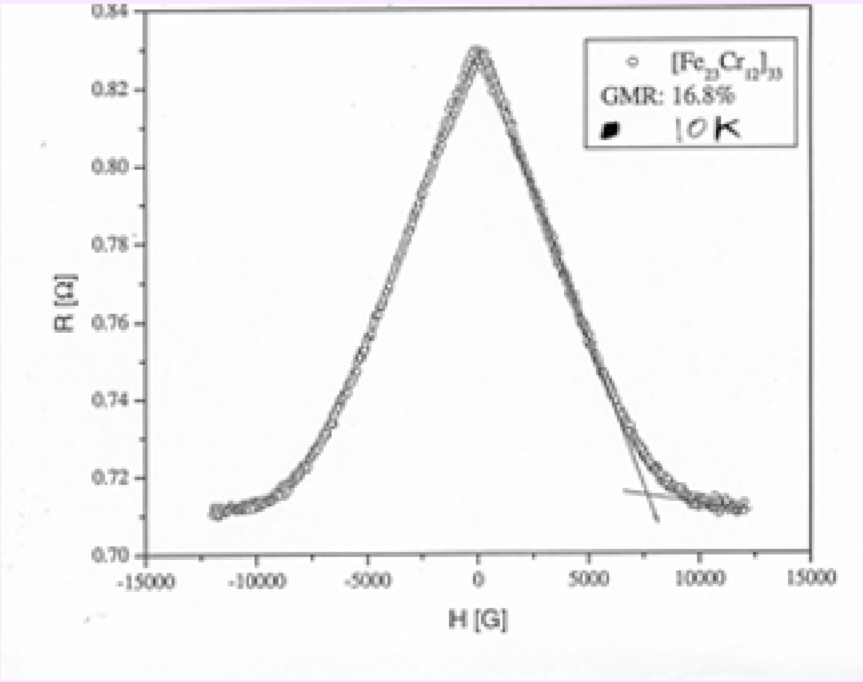
1. Fe/Cr giant magnetoresistance multilayers
2. Amorphous Si and RE-Si alloys
3. Antiferromagnetic CoO nanoparticles and thin layers

Fe/Cr multilayers: GMR

Fe/Cr: antiferromagnetically coupled Fe layers

Giant negative magnetoresistance

(23Å Fe/12Å Cr)$_{33}$: total thickness of 1000 Å (maximum GMR)



Comparison samples of 1000 Å Fe and 1000 Å Cr

What can specific heat tell us about GMR? electron density of states (DOS)

Quantum well states? Seen in photoemission and other studies

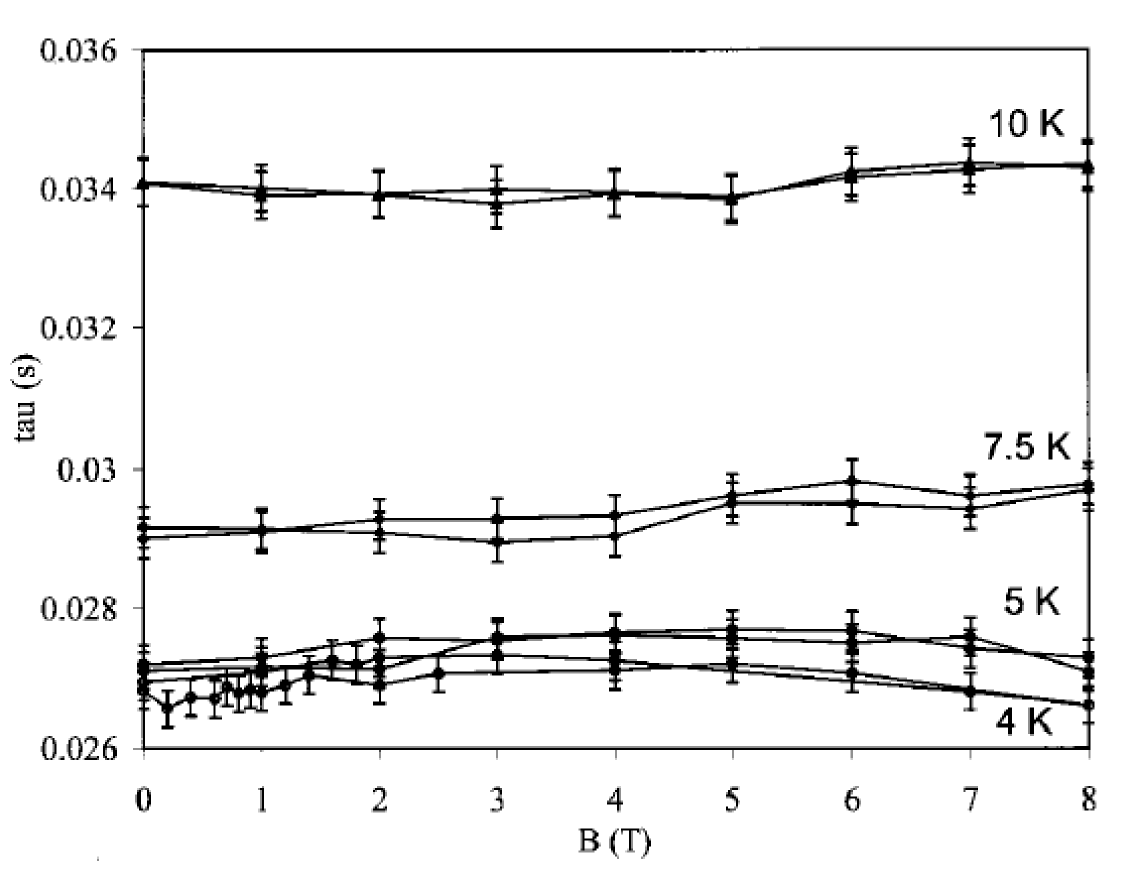
Cr spin density wave? (not likely in thin Cr layers)

Spin density wave reduces $N(E_F)$ by ~ factor of 3-4

Low temperature specific heat $C \sim \gamma T + \beta T^3$; $\gamma \sim N(E_F)$

Is GMR purely a scattering effect or do changes in electronic density of states $N(E_F)$ play a role?

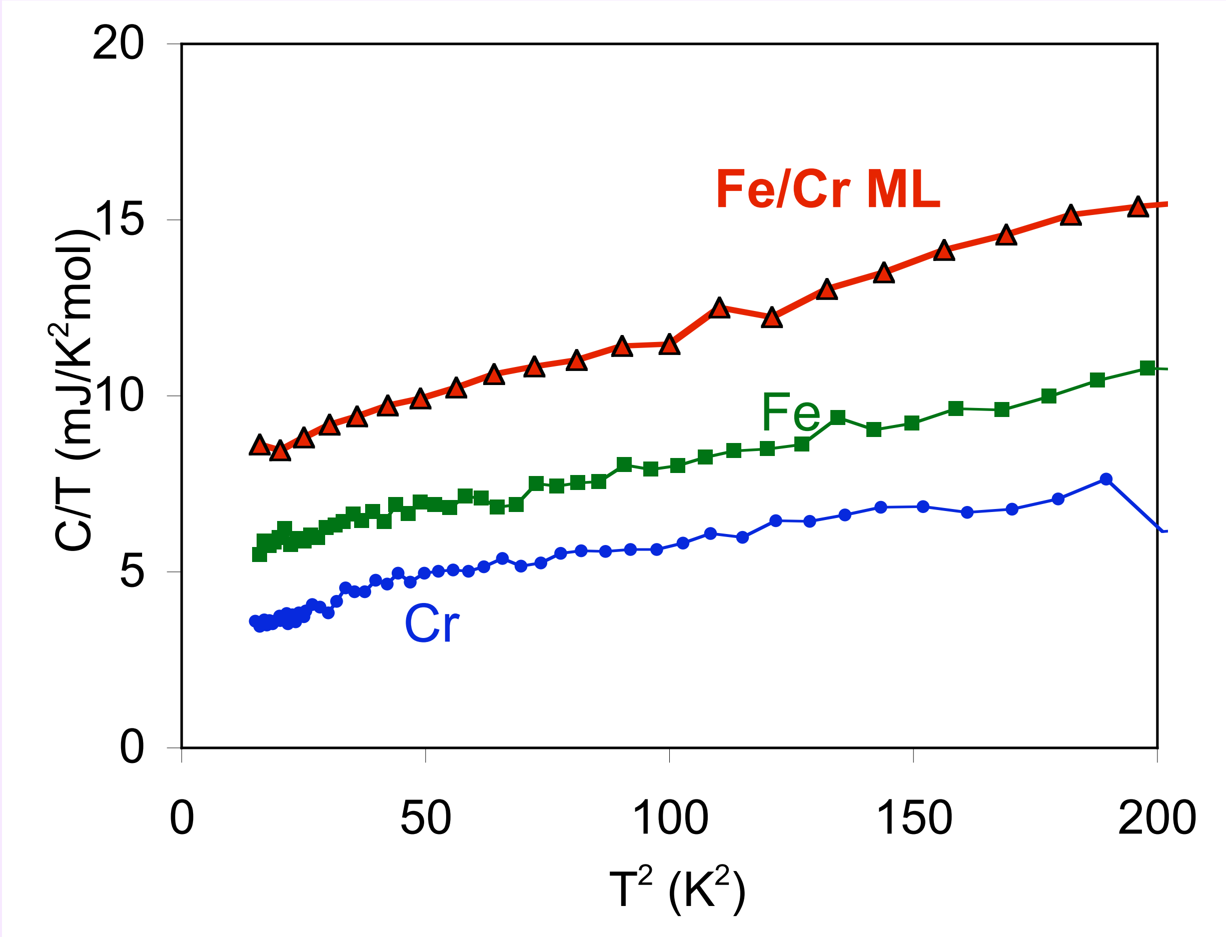
Fe/Cr multilayers: no field dependence



 proportional to C: independent of field

GMR not likely to be related to DOS effects

Fe/Cr multilayers: low Temp C_p gives electronic density of states (DOS)



C_p shows $□$ DOS twice as large for multilayer as for Fe or Cr

Interfacial alloying?? Quantum interference??

Phonons also affected: $□_D$ Fe/Cr ~ $□_D$ Cr ~ $□_D$ Fe

Fits to low T specific heat

TABLE I. Result of the least square fit of Eq. (3.1) to the specific heat heat data of Fig. 4. Bulk values are given in paranthesis.

Sample	t [Å]	γ [mJ/K^2 mol]	Θ_D [K]
Cr	1035	3.2 ± 0.3 (1.4^a,3.5^b)	415 ± 13(610^c)
Fe	1050	5.4 ± 0.4 (4.95^c)	415 ± 13(460^c)
Fe/Cr MML	1159	8.7 ± 0.7	356 ± 10

[a]Magnetic Cr, from Ref. 4.
[b]Non-magnetic Cr, from Ref. 4.
[c]From Ref. 18.

Cr non-magnetic

Fe/Cr ML enhanced: quantum well states? Interface alloy? Substantial softening for Cr, Fe/Cr ML: Debye temp ~same!

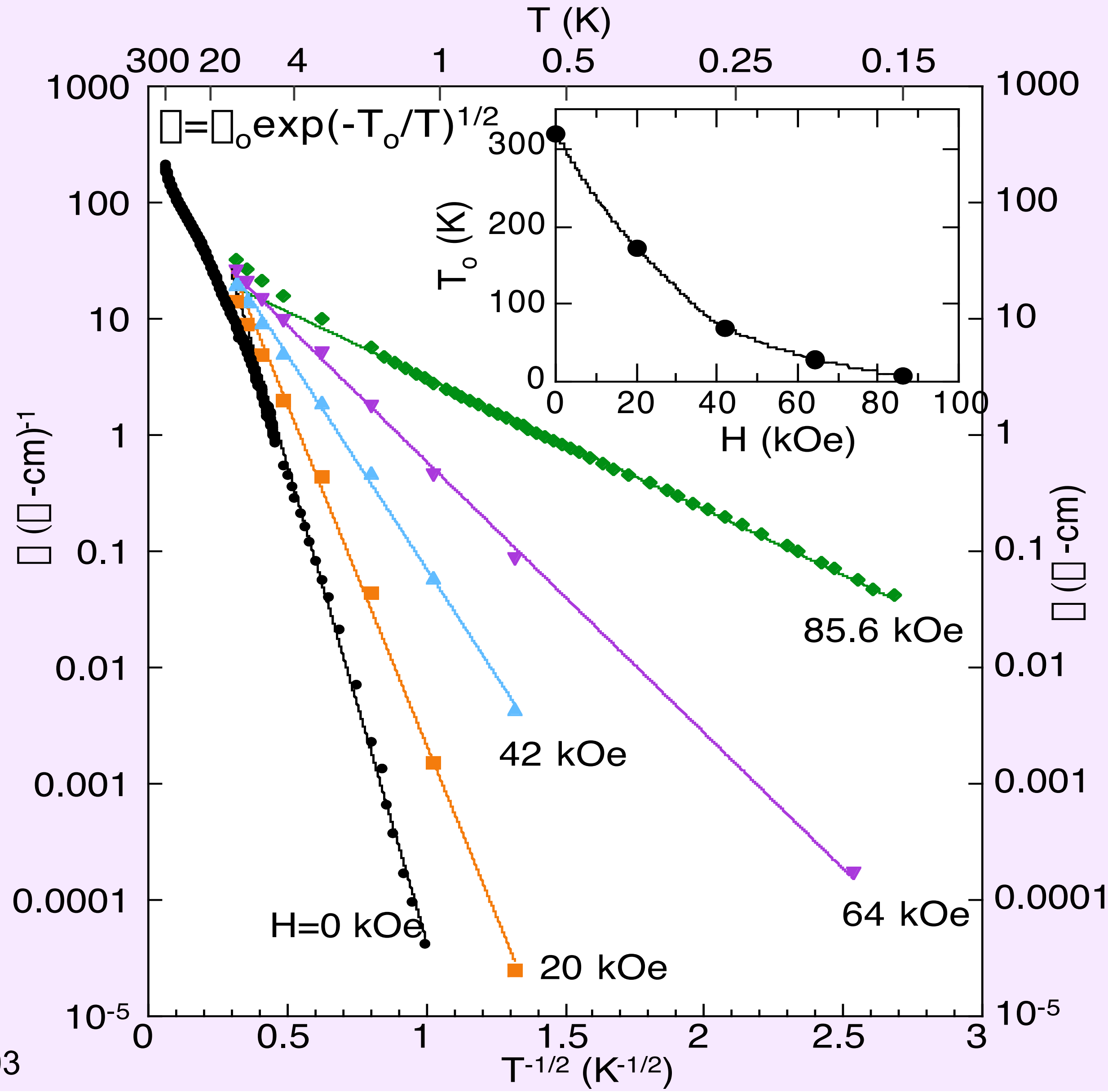
Amorphous RE-Si alloys: a-Gd_xSi_{1-x} and a-Y_xSi_{1-x} (0.1<x< 0.2; Metal-Insulator transition at 0.14)

Gd: $4f^7 5d^1 6s^2$
Y: $4d^1 5s^2$

Enormous MR (magnetoresistance)

Because of interaction between delocalized electron spin and core spin; depends on their relative angles

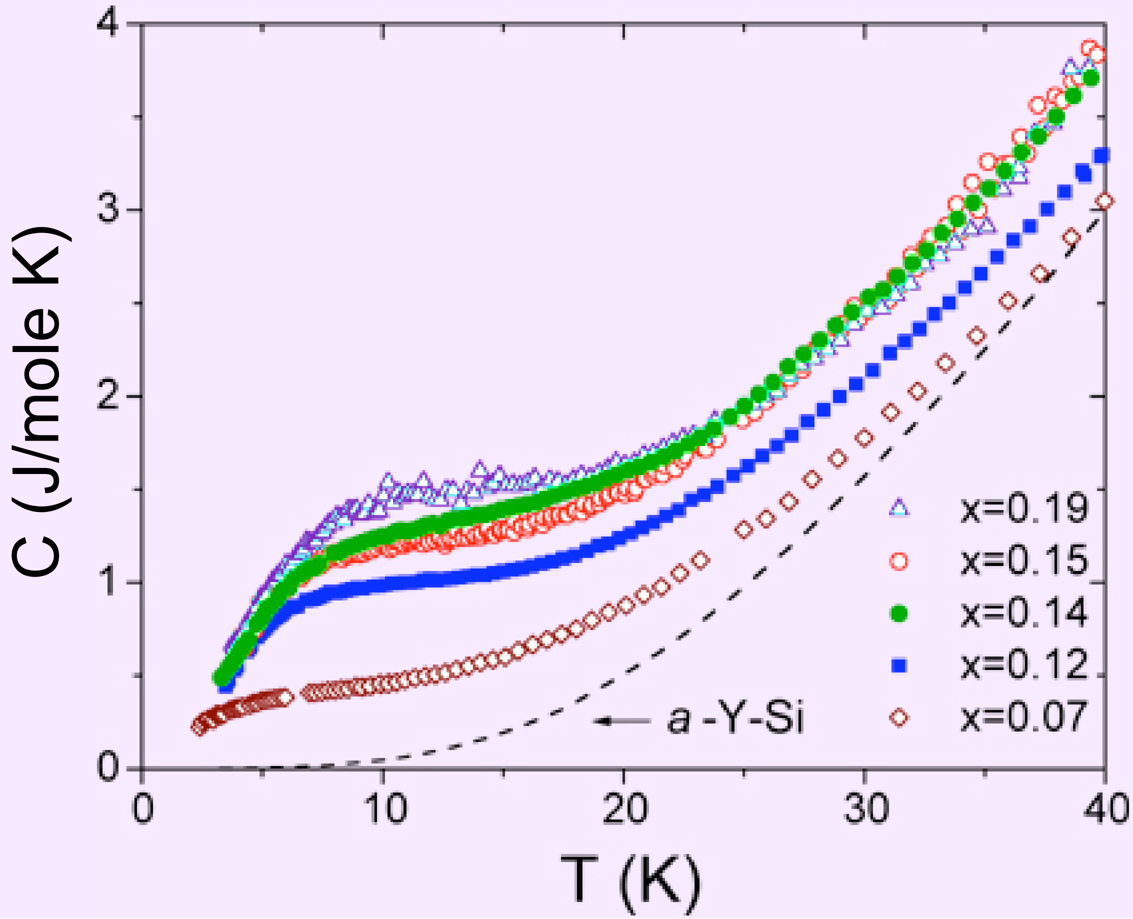
Magnetic field aligns core spins



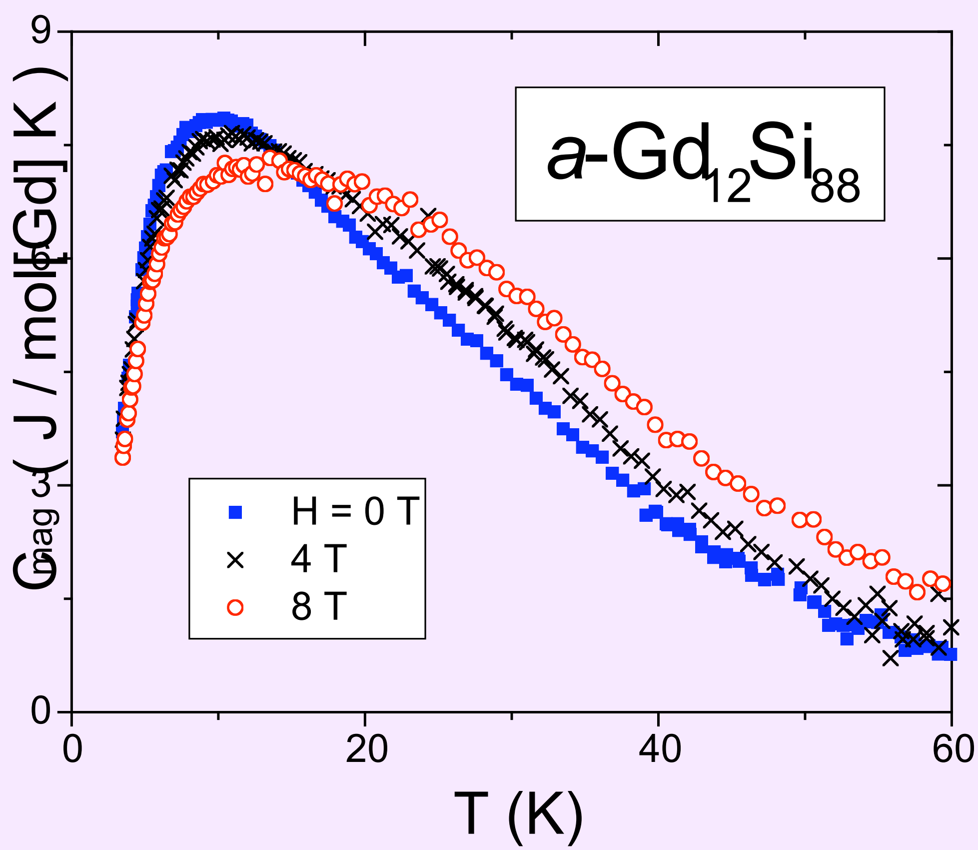
Hellman et al, various papers 1996-2003

Specific heat of a-Gd-Si

Spin glass freezing gives large signature
Has more entropy than Rln2J+1= Rln8
Due to conduction electron spins??
Excess heat capacity (Gd-Si minus Y-Si) persists to high T like MR

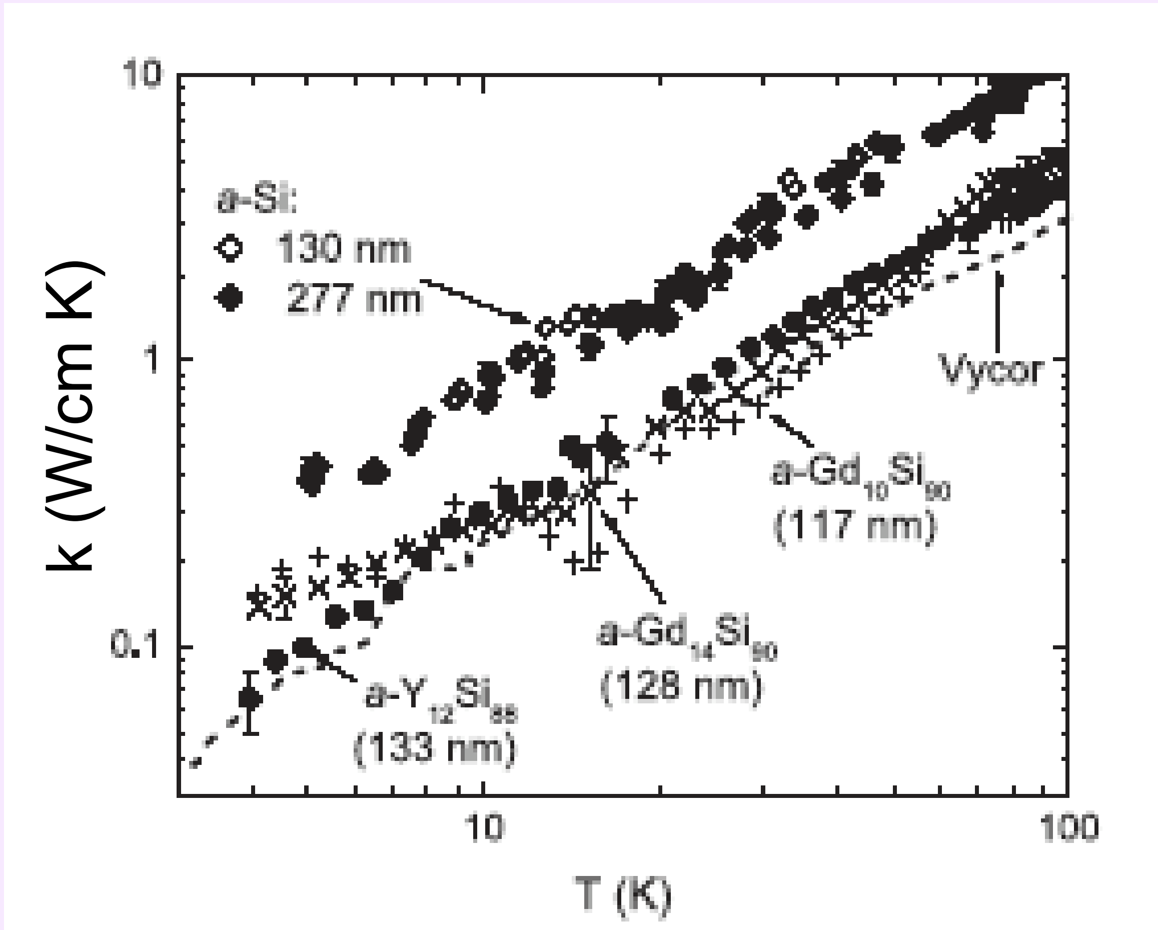


Specific heat of a-Gd-Si: effect of magnetic field also extends to high temperature



With increasing magnetic field, C_{mag} shifts up in temperature
Effect of magnetic field very small due to strength of interactions

Thermal Conductivity of a-Si and a-RE-Si alloys (sample covers whole membrane area: k from)

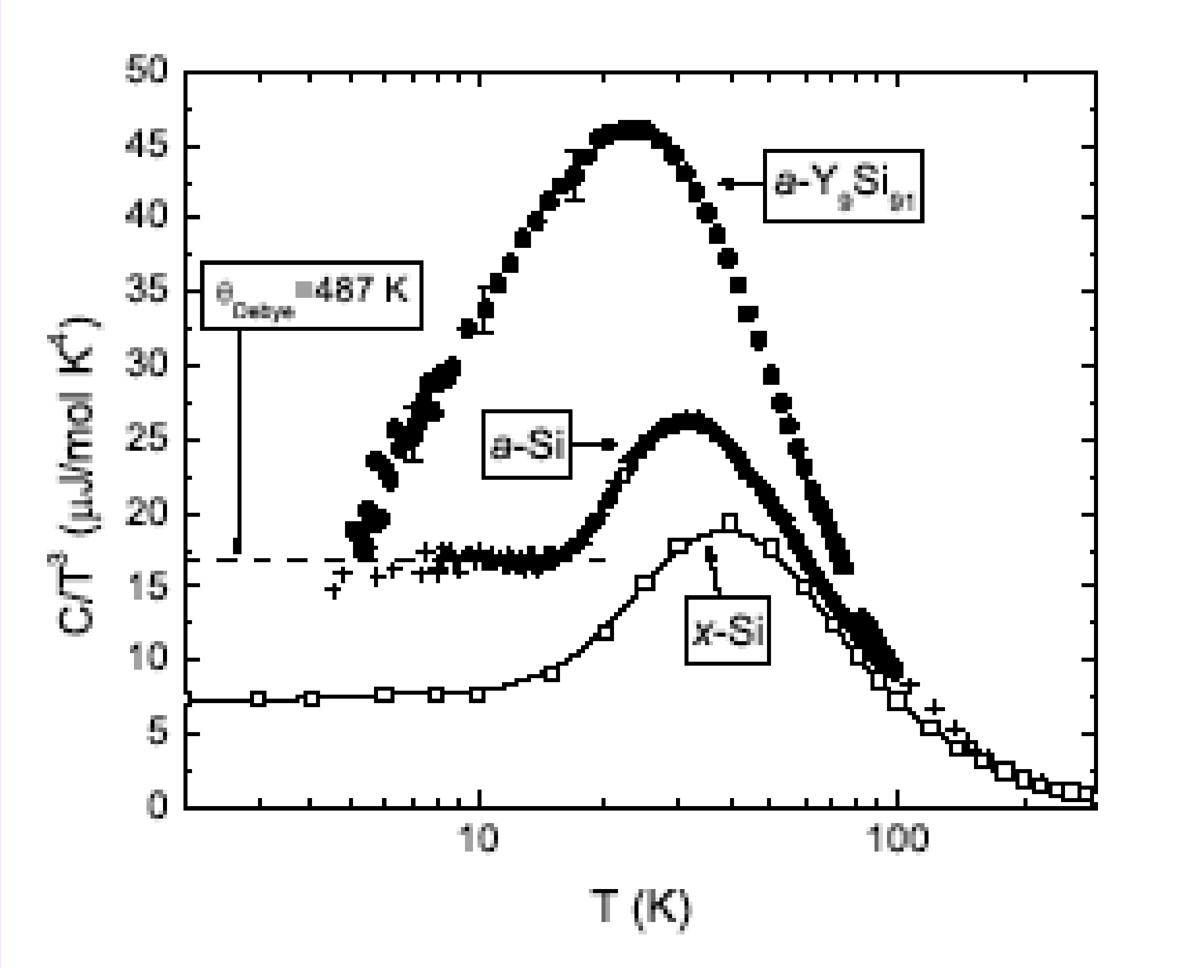


Thermal conductivity of a-Si: no sign of the usual plateau

Added RE ions: decreases k over very wide temperature range

In analogy to filled skutterudites, RE "rattles" in Si cage, reducing k

Heat capacity of amorphous Si (and SiN): anomalous amorphous materials



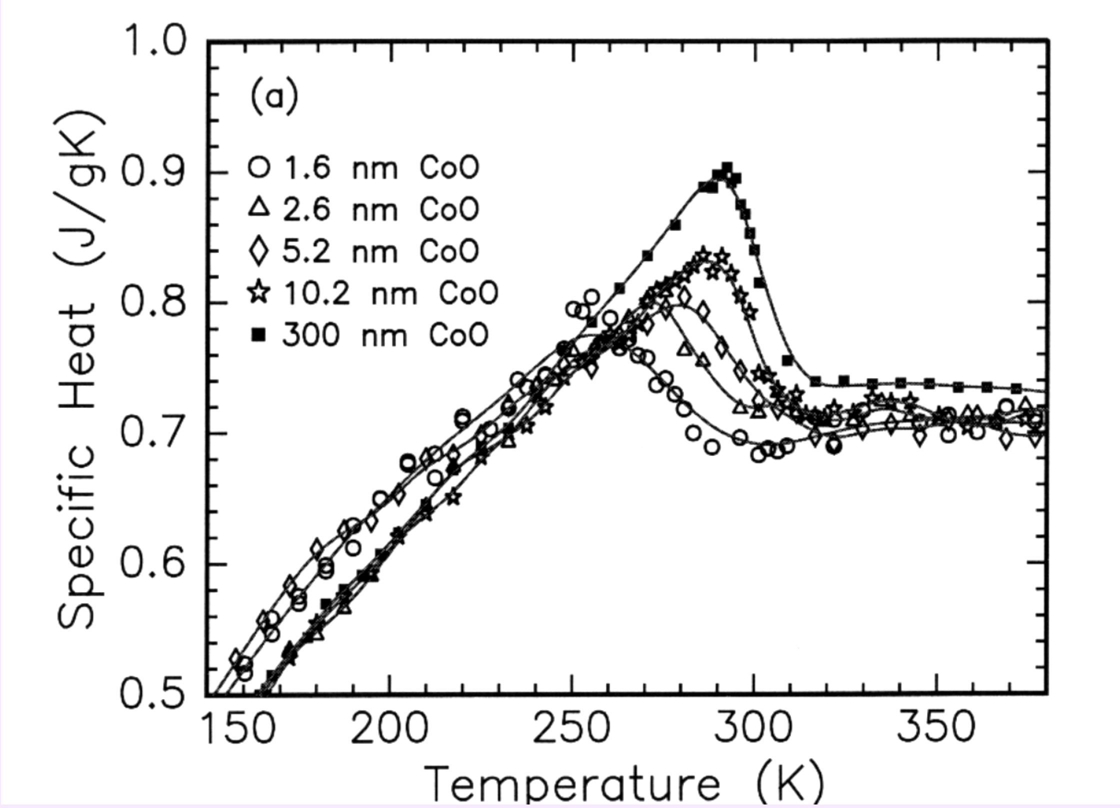
B. L. Zink, B. Revaz, R. Pietri, F. Hellman, PRL, to appear

No sign of the usual greatly enhanced non-Debye low T specific heat C
Likely due to the overconstrained nature of the tetrahedral Si bonding

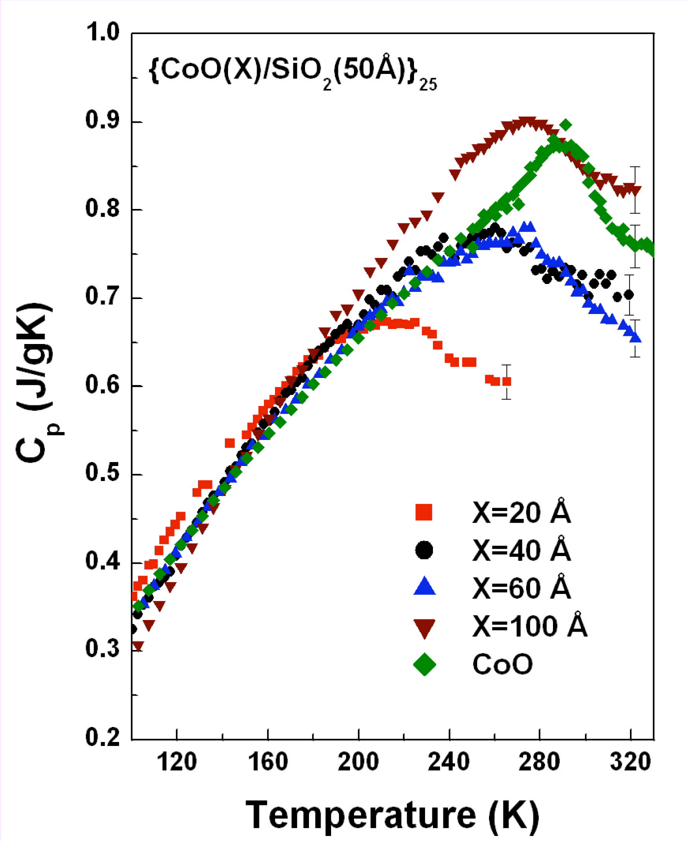
Antiferromagnetic CoO thin layers and nanoparticles

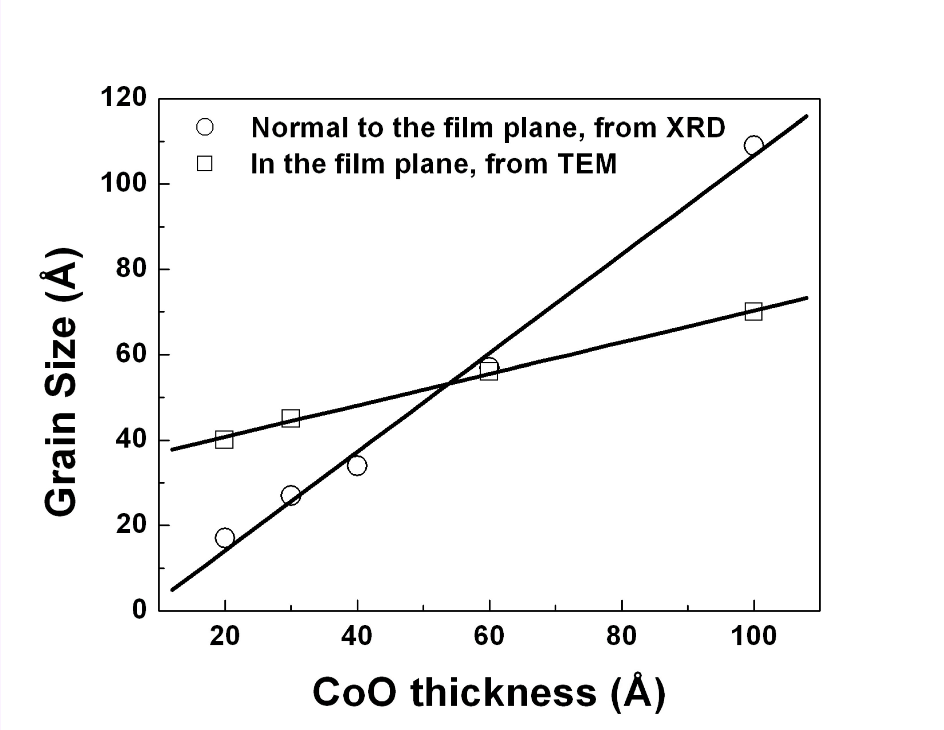
- 2D layers in multilayers
- 0D grains or particles (in matrix or granular)
- Study effects on Neel temperature, on magnons, phonons

CoO/MgO multilayers:
very little suppression of T_N
even at 1.6 nm



$CoO/a\text{-}SiO_2$ multilayers: effects of small grain size



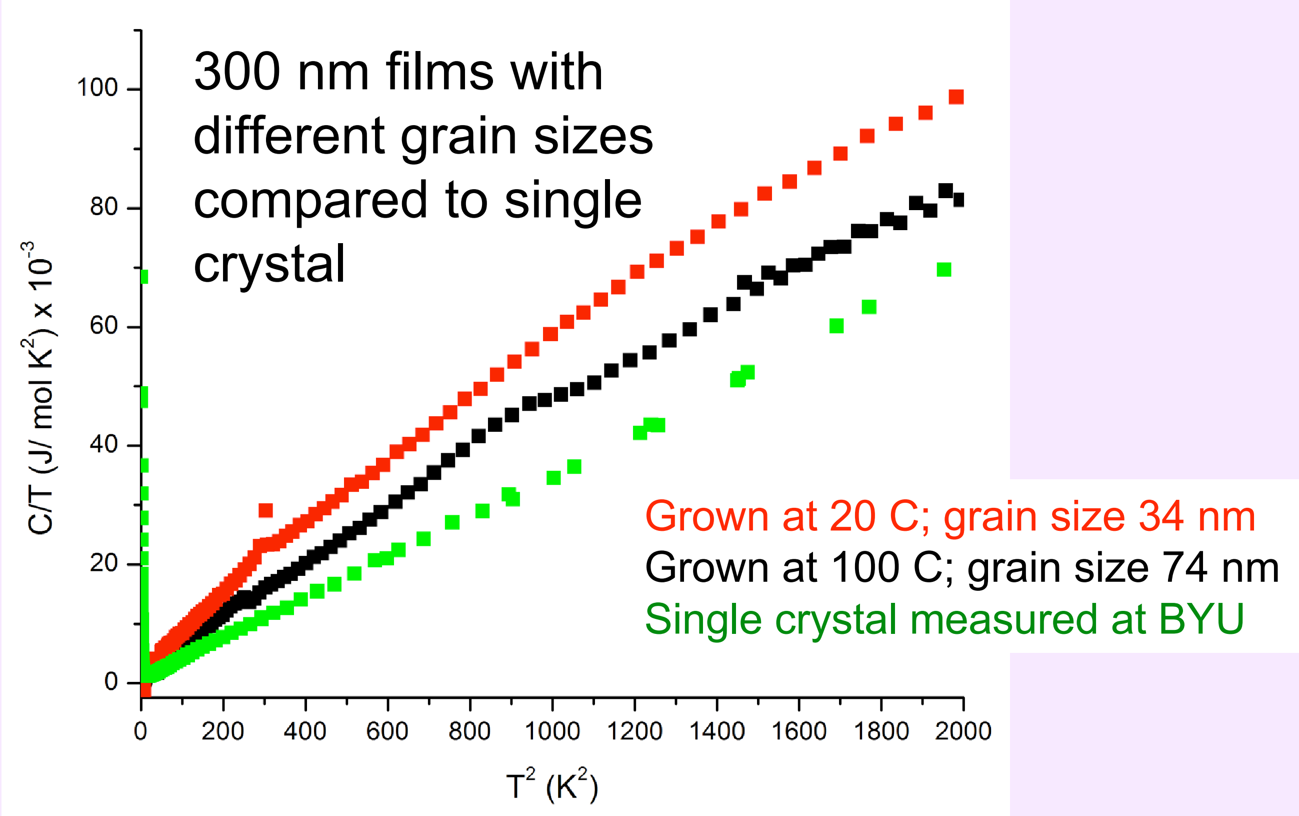


CoO layered with a-SiO_2: T_N strongly suppressed and broadened

TEM shows thin CoO on a-SiO_2 is amorphous!

"Finite size effects" not always intrinsic! Here, dominated by structural disorder

CoO: low temperature C_p: the effect of grains on phonons (preliminary results)



- Phonon softening at low temperature in samples with smaller grain size
- Small linear term also seen; likely due to disorder at grain boundaries
- Increased entropy: affects thermal stability of phases (collaboration with Alex Navrotsky, Brian Woodfield and Julie Boerio-Goates)

Conclusions

1. Si-micromachined membrane based calorimetry devices can be used to measure C_p of films and tiny crystals (micrograms) from 1-550K, 0-8T
   Also used for measuring thermal conductivity, thermopower
2. Fe/Cr giant magnetoresistance multilayers
   - Enhanced electron density of states (2x Fe/Cr average)
   - No dependence (<1%) on magnetic field
3. Amorphous RE-doped Si alloys, amorphous Si, amorphous SiN
   - Specific heat: spin glass freezing, excess entropy
   - Weak field dependence due to strong RKKY-like interactions
   - *a*-Si and *a*-SiN: quite different C and k than "usual" amorphous materials. Strongly bonded overconstrained network
   - Thermal conductivity of RE-doped *a*-Si strongly reduced compared to a-Si
4. Antiferromagnetic CoO nanoparticles and thin layers
   - Suppression of Neel temperature
   - Phonon softening- how common in films?
5. Future directions (in progress):
   - Calorimetry for international fusion reactor (ITER); for high magnetic fields; smaller samples (scaled down devices); lower T (0.3K); higher T (800 K)