ellman Lab

Calorimetry of magnetic materials: films, nanocrystalline materials

BERKELEY LAB

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LBL Materials Sciences Division

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)
S. Barriga (undergrad)

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:

M.-C. Cyrille, I. K. Schuller, Z. Boekelheide, E. Helgren, D. Cooke, D. Queen, A. Fathalizadeh, M. Carey, N. Leon (Fe/Cr multilayers, Cr and Fe films)

Y. J. Tang, J. Boerio-Goates, B. Woodfield, A. Navrotsky, K. Takano, A. Berkowitz, D. Cooke (CoO)

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Calorimetry of nanostructured magnetic materials

Magnetic and thermodynamic properties strongly affected by nanoscale structure, e.g. multilayers, nanocrystalline materials (grain boundaries), nanocomposites

Length scales are intrinsically short (nm) hence characterization is difficult but crucial

Magnetic nanostructure central to modern applications, e.g. magnetic recording

Modern magnetometry is sensitive enough to study tiny volumes of material

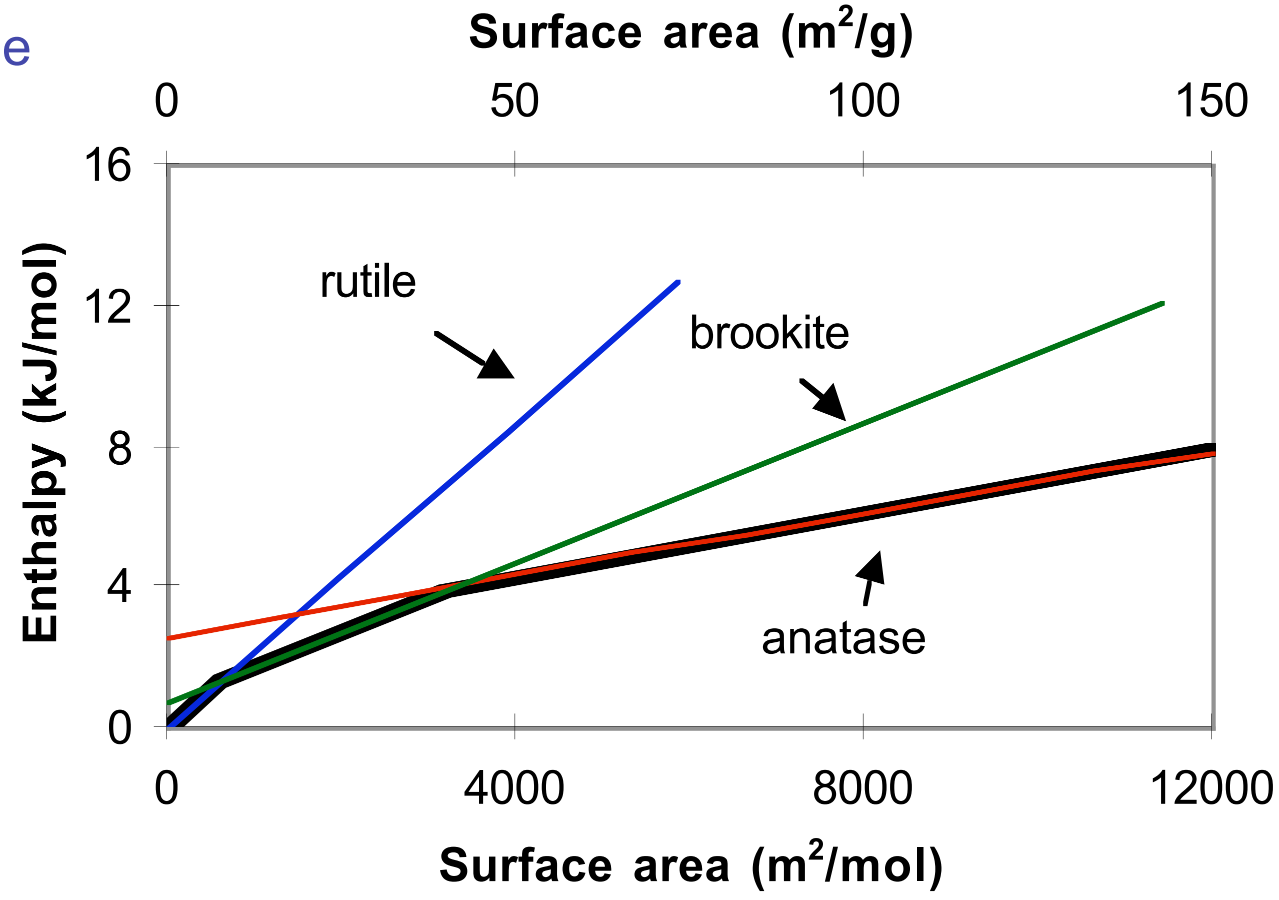
Calorimetry traditionally has not been: *Si micromachined nanocalorimeters*

Thermodynamics: nanostructure may stabilize non-equilibrium phases

Heat capacity gives us phase transitions; electron, phonon DOS; crystal fields; entropy

Thermodynamics of nanostructured materials

Enthalpy of TiO_2 polymorphs vs inverse grain size (Alex Navrotsky group, UCDavis)



Small Sample Calorimetry

Basic calorimetry: heat Q into sample, measure temp. rise $c = Q/\Delta T$

Problem for small samples:

1. Heater, thermometer, sample platform all have heat capacity ("addenda") – swamps sample

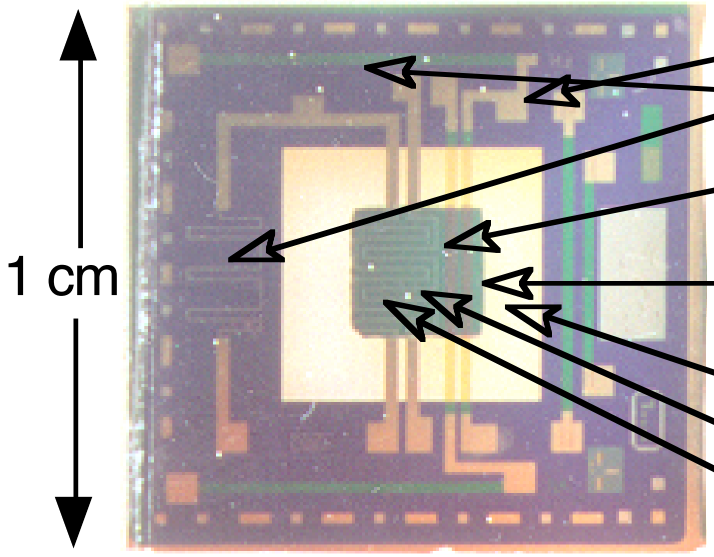
   Solution: thin film heater, thermometers, and sample platform: thin membrane of low stress *a*-Si-N (*a*-Si-N also has a high Debye temp).

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.

Micro/nanocalorimetry: overview (fabricated in the UCB Microlab)



Pt contact pads for electrical bonding

matching thermometers on Si frame

low temp thermometers (a-Nb-Si or B:poly Si)

sample and thermal conductivity layer
(on back of membrane)

α-SiN membrane 180 nm thick (now 30 nm)

heater (Pt)

high temp thermometer (Pt)

Allows us to make unique measurements: heat capacity of

- μg and sub-μg (films ~100 nm thick)
- Evaporated/sputtered films; powders; tiny crystals;
- Wide temperature range 1-500K (to date)
- Magnetic field (0-8T to date) *in situ*

Thermal conductivity

Thermopower

APS-Keithley Instrumentation Award 2006

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)

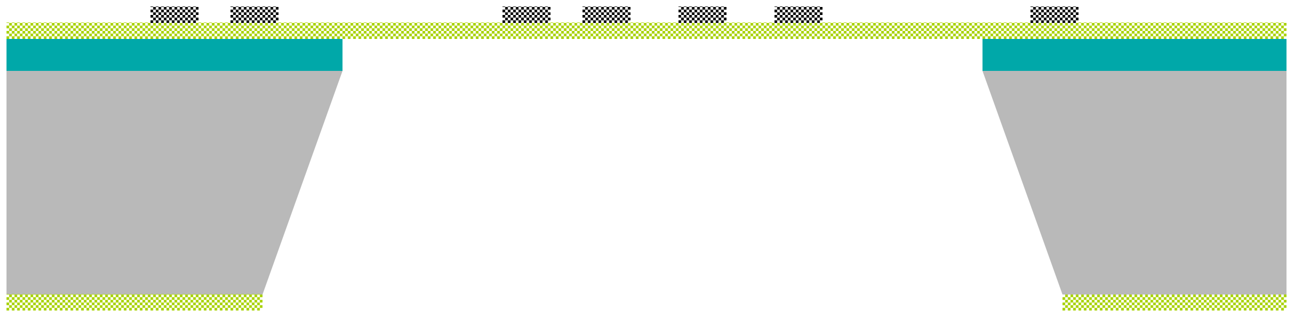
Microcalorimeter Construction

180 (now 30) nm low-stress *a*-SiN$_x$
(LPCVD @ 835°C)

Microcalorimeter Construction

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

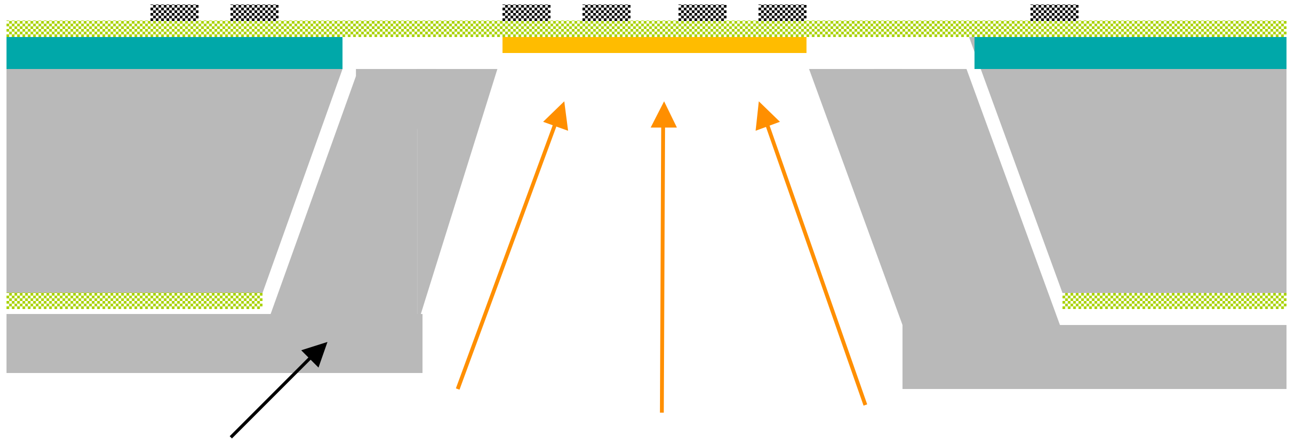
Microcalorimeter Construction



Form Membrane (180 nm thickness, 0.5cm x 0.5cm; now 30 nm, 0.2cm x 0.2 cm) with KOH anisotropic wet Si etch

Thermal Conduction Layer

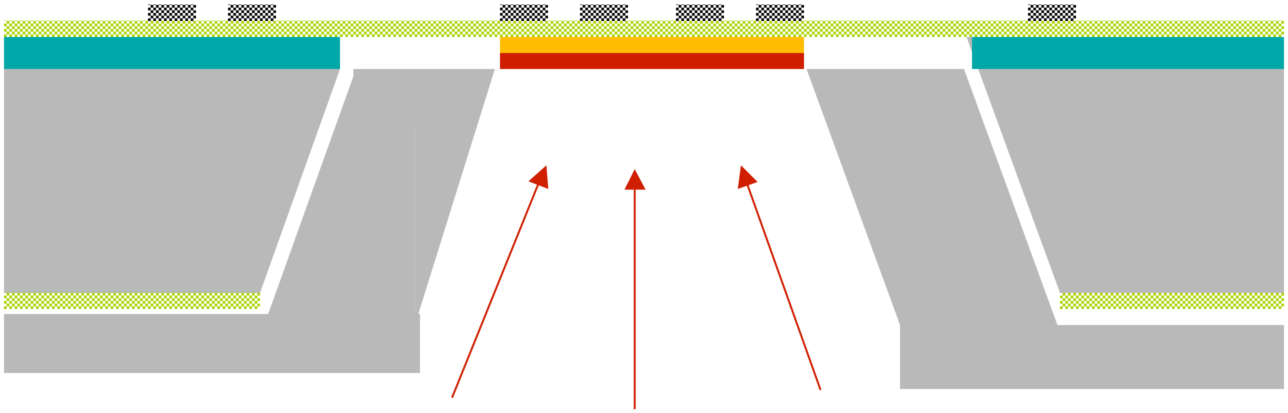
Deposit Thermal Conduction layer
~180 nm (now 30 nm) of Al, Cu, Au, Ag



Micromachined Shadow Mask

Sample: Heat Capacity, Vapor Deposited Films

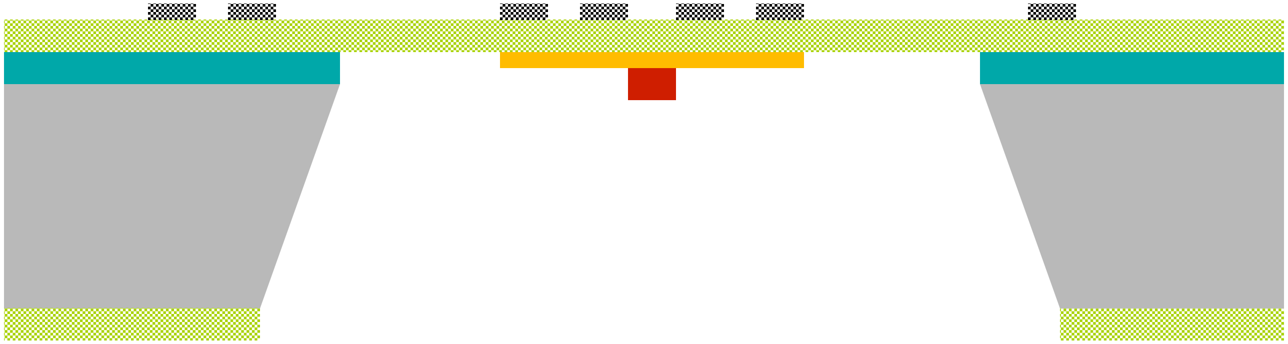
180 nm vapor deposited sample (~10 μg) (now 30 nm, ~1 μg)



Deposit sample only on
conduction layer

Or bulk crystals

~200 μg attached with Indium or silver paint (measure In/ silver paint separately)



Measuring Specific Heat: Small ΔT Relaxation Method

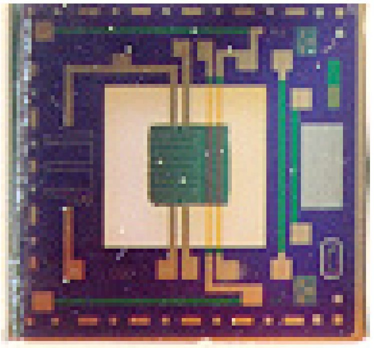
Small ΔT Relaxation Method:

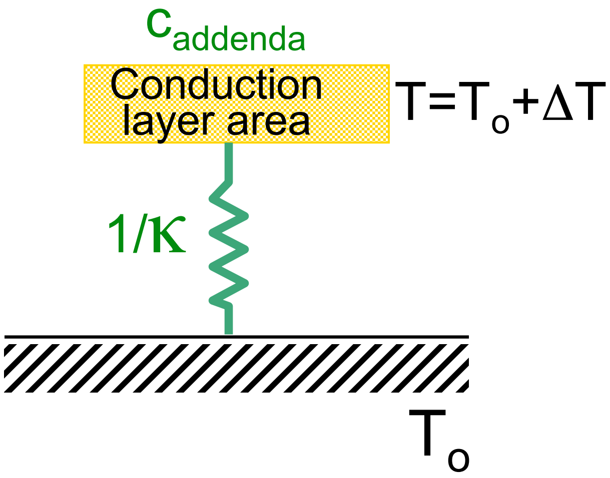
1) Power P into sample heater
2) Measure ΔT in steady state

$$\kappa = P/\Delta T$$

3) Time t=0, turn off heater:

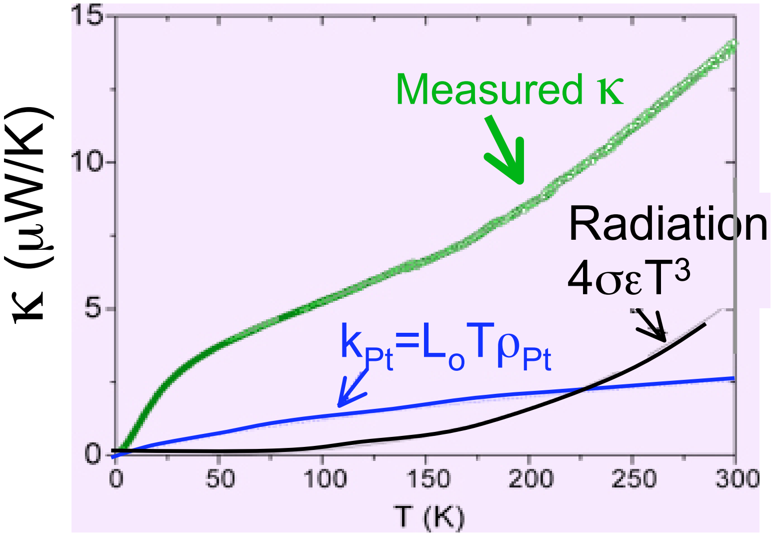
$$\Delta T\, e^{(-t/\tau)}$$



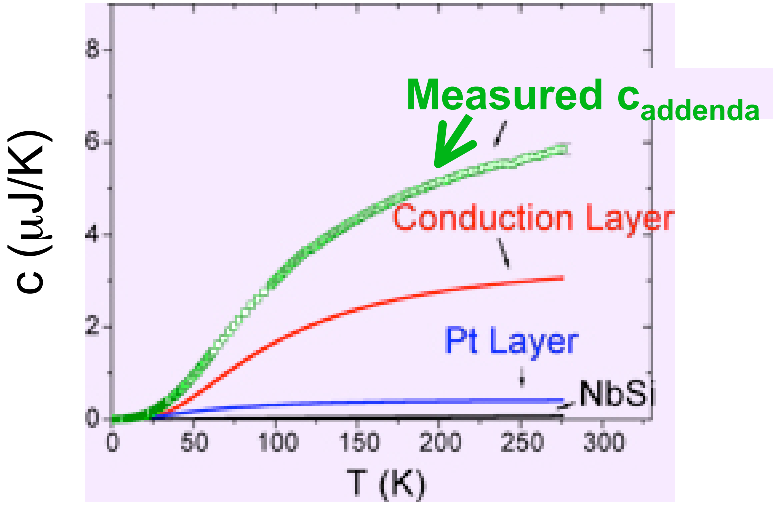


$$\boxed{c_{addenda} = \kappa\,\tau}$$

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



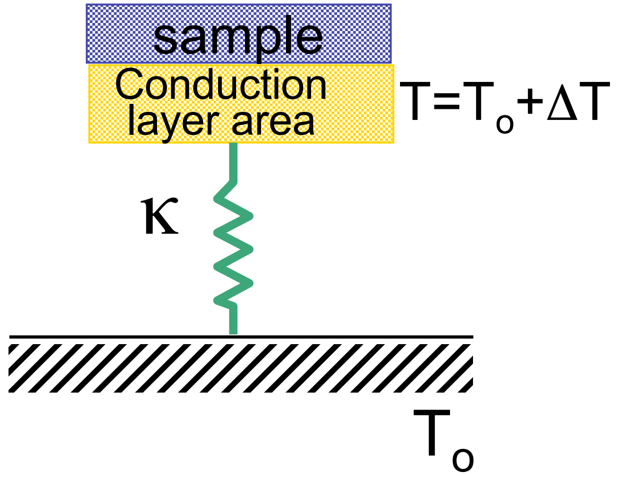
$$c_{addenda} = c_{Si\text{-}N} + c_{cond} + c_{Pt} + c_{NbSi}$$



Measuring Sample Specific Heat: repeat measurement with sample

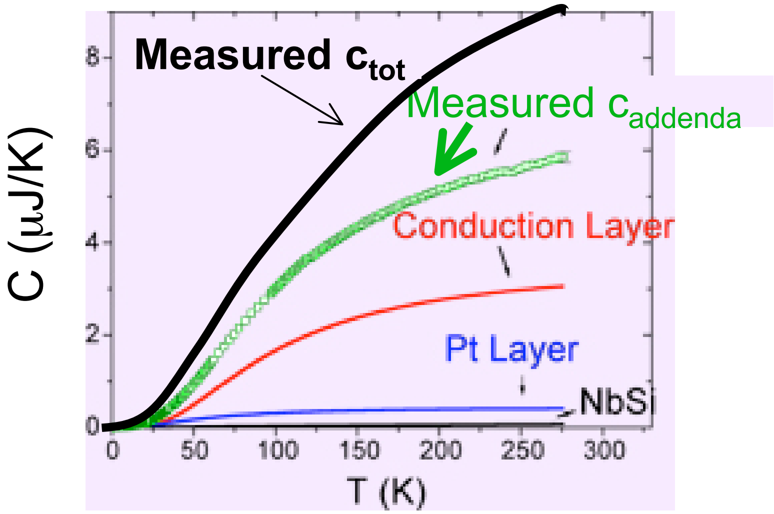
Small ΔT Relaxation Method:

1) Heat Q into sample heater
2) Steady state: $\kappa = Q/\Delta T$ (measure, but unchanged)
3) Time t=0, turn off heater: $\Delta T\, e^{(-t/\tau')}$

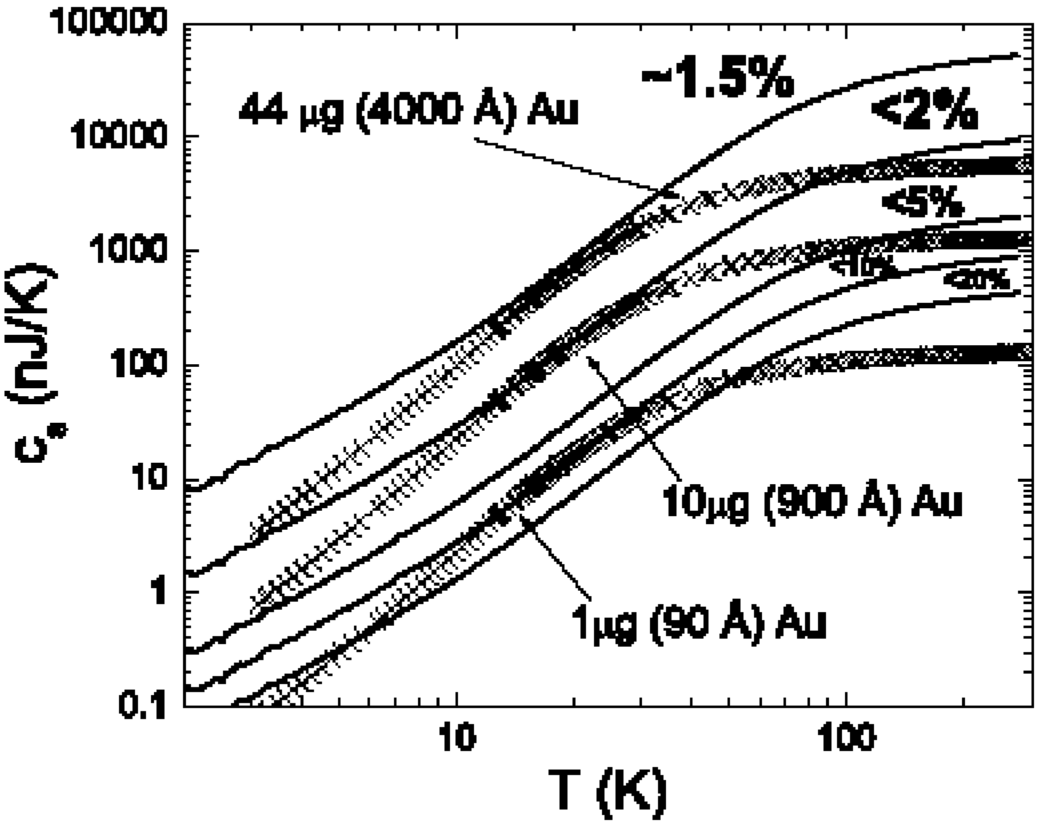


$$\boxed{c_{total} = \kappa\,\tau'}$$

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



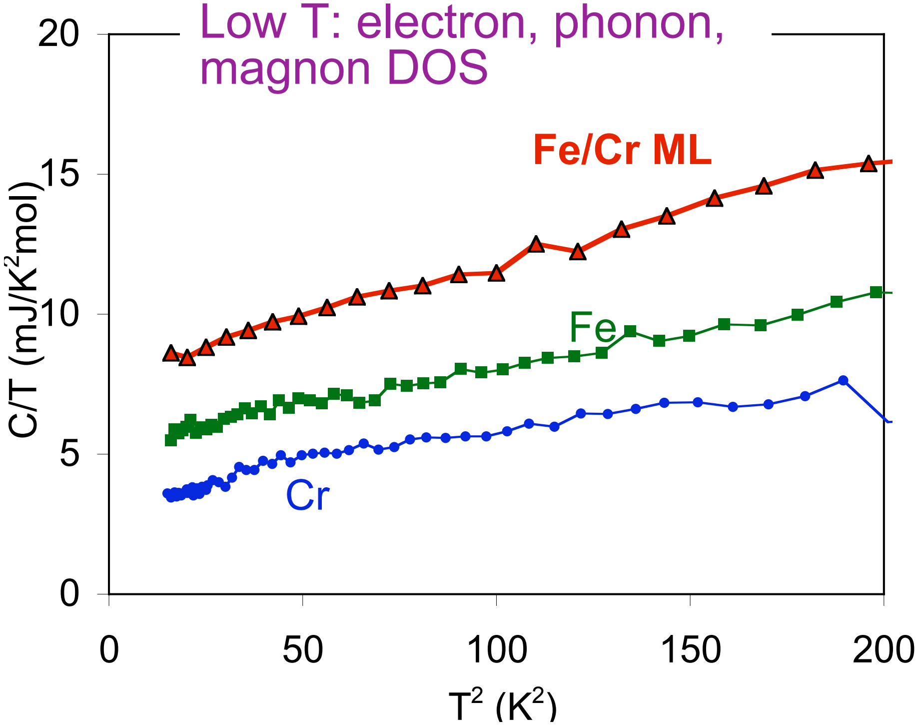
Thermal simulations: Membrane contributions to background, precise error bars



Accuracy of measurement depends on sample size and temperature; 2% usually possible

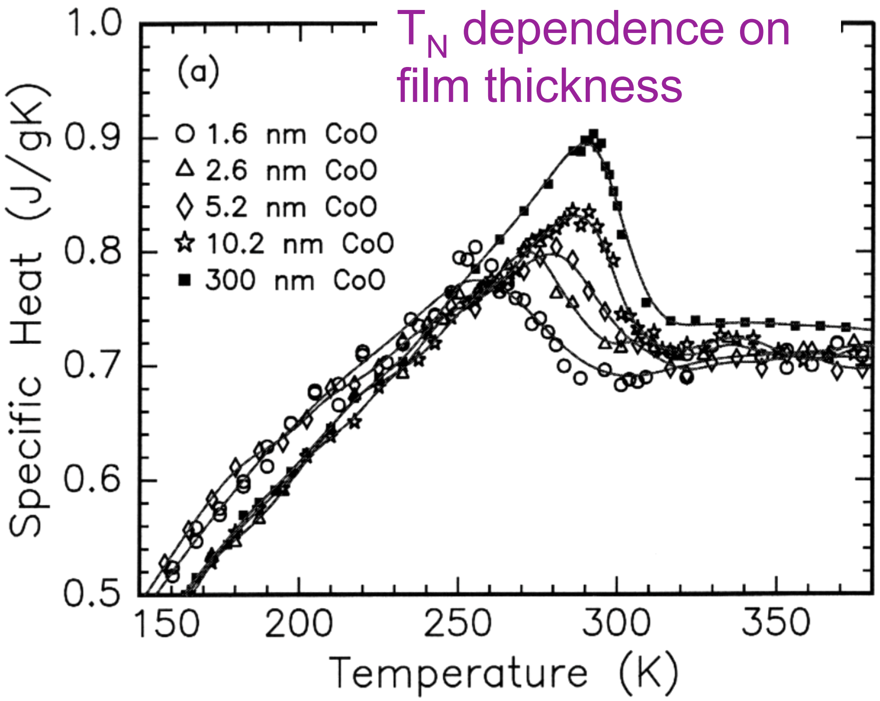
Calorimetry of nanostructured materials: two examples

Giant magnetoresistance Fe/Cr multilayers and Cr films



Low T: electron, phonon, magnon DOS

Antiferromagnetic CoO/MgO multilayers



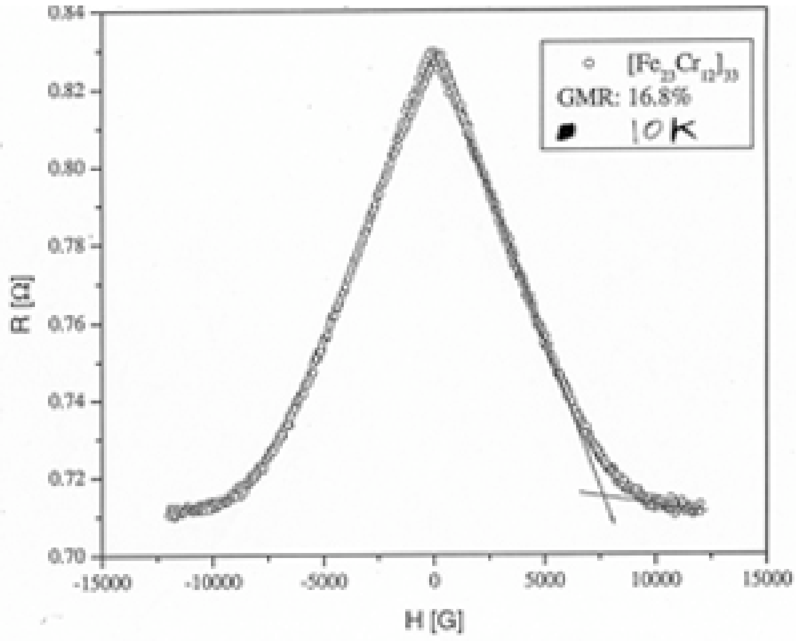
T_N dependence on film thickness

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)



Collaboration with I. K. Schuller, Matt Carey

Comparison samples of 1000 Å Fe and 1000 Å Cr

What can specific heat tell us about GMR? Electron density of states (DOS) at E_F

Quantum well states? Seen in photoemission and other studies

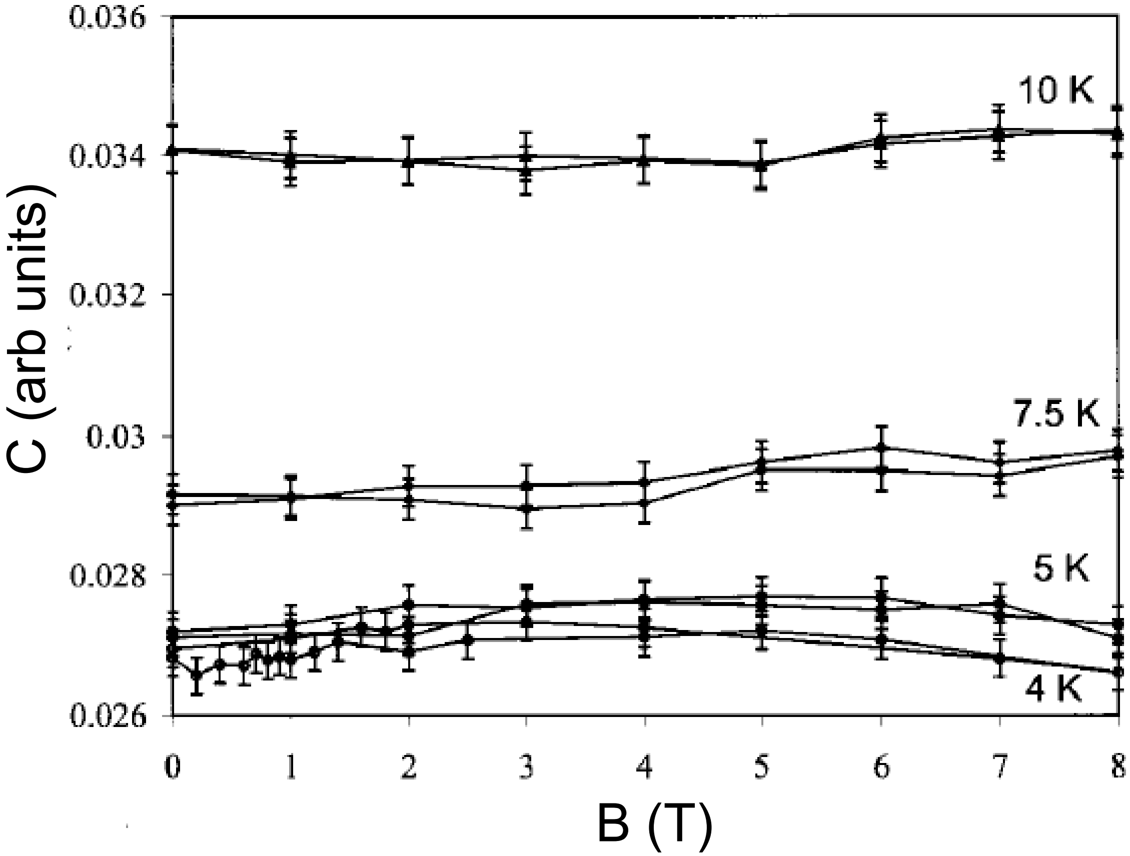
Cr spin density wave?

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

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

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



τ proportional to C: independent of field

⟹ DOS independent of field

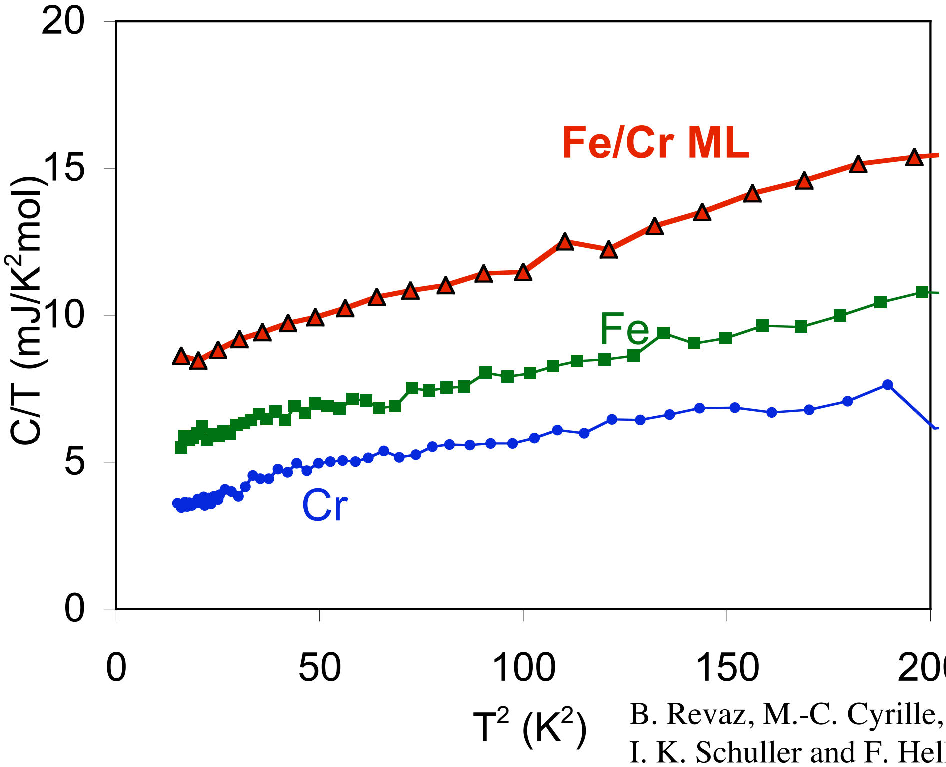
GMR not likely to be related to DOS effects

Giant Magnetoresistance Fe/Cr multilayer: Low T C_p gives electron density of states (DOS)

$C/T \sim \gamma + \beta T^2$

γ ~ electron $N(E_F)$

β ~ phonon softness ~ $1/\theta_D^3$



B. Revaz, M.-C. Cyrille, B. Zink, I. K. Schuller and F. Hellman, Phys. Rev. B **65**, 944171 (2002).

γ large for Cr film: probably non-magnetic

γ twice as large for multilayer as for Fe or Cr

- Interfacial alloying?? Quantum well states??

Phonons also affected

- Substantial softening for Cr & Fe/Cr ML: θ_D Fe/Cr ~ θ_D Cr ~ θ_D Fe

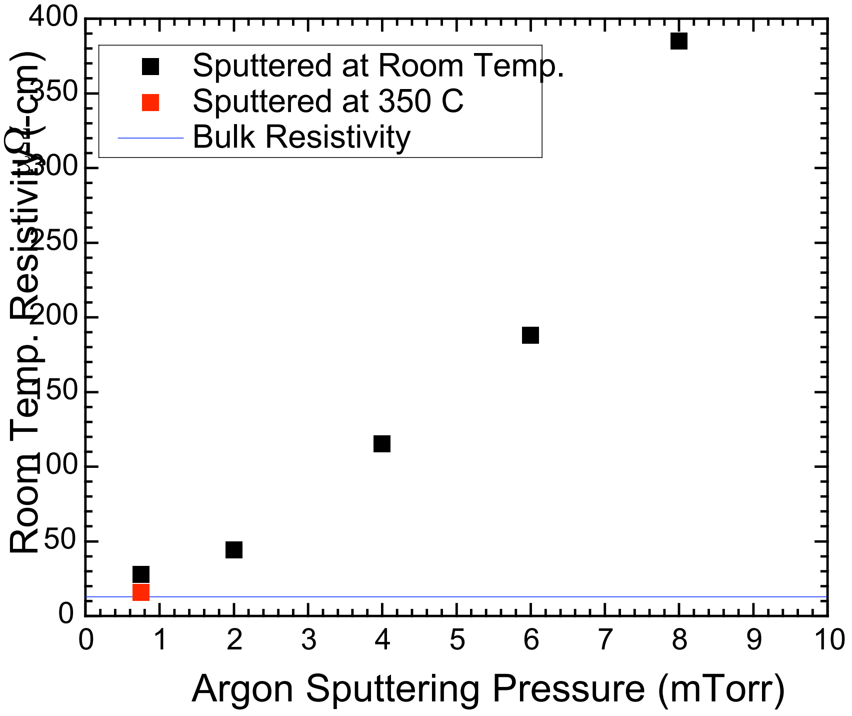
Specific heat of Cr films

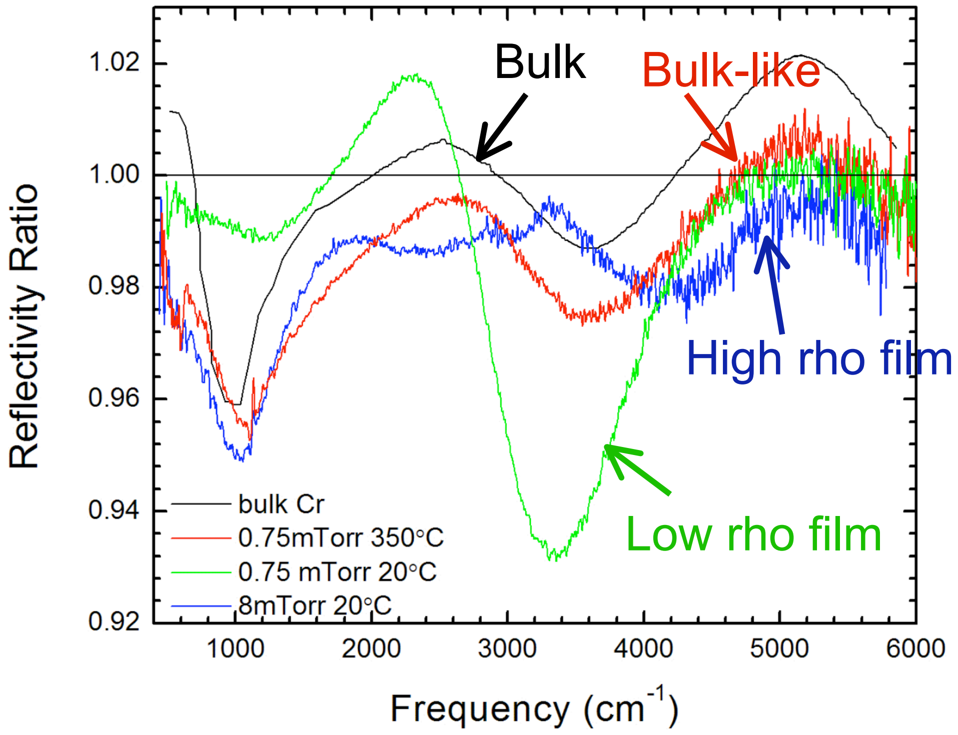
Cr films also have larger γ than expected

Resistivity of Cr varies by orders of magnitude with preparation conditions, unlike similar structure Fe

TEM and X-ray shows drastic changes in grain structure

Optical reflectivity shows changes in spin density wave structure



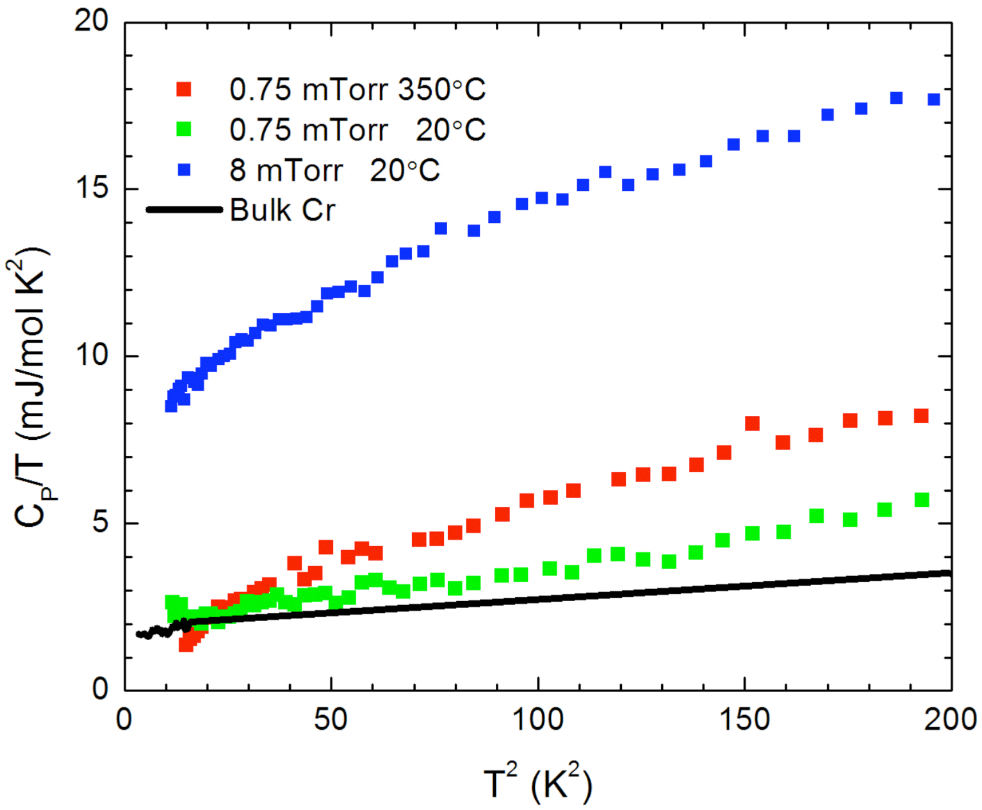


Low T specific heat of Cr films

High resistivity films (grown at 8 mTorr Ar sputtering pressure) have very high γ, electron density of states at E_F, much higher than calculated or measured for non-magnetic Cr

Disorder broadening?? (E_F lies in minimum of electron DOS)

Effects also seen in phonons: softening of lattice

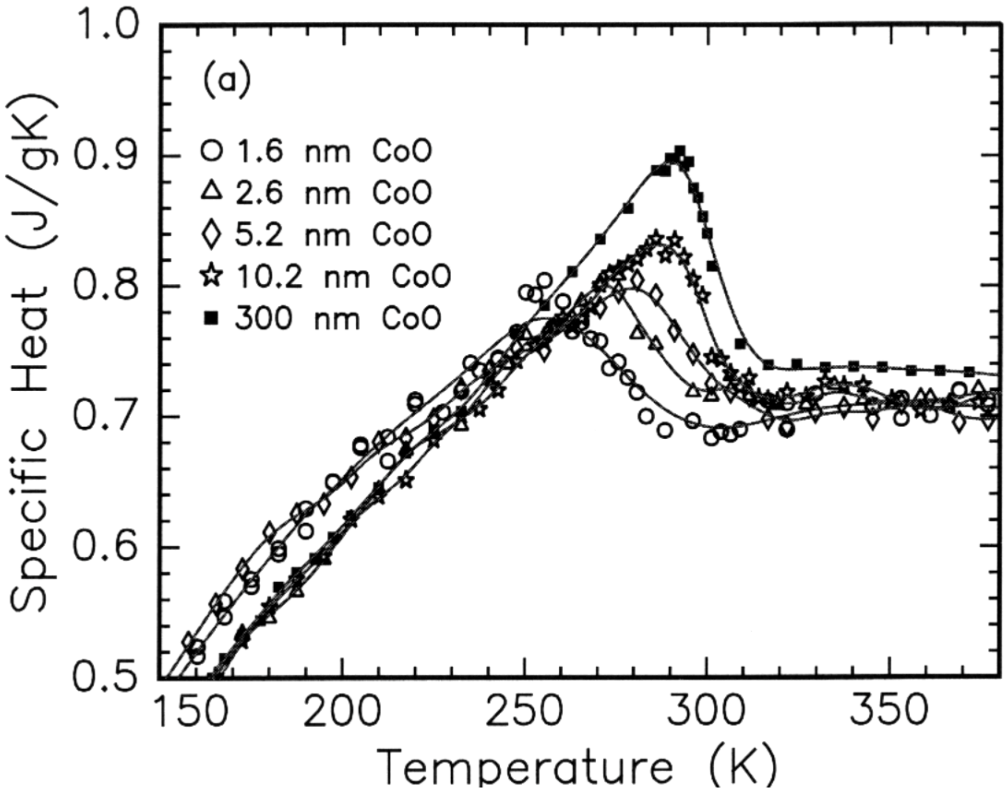


P (mTorr)	T (°C)	γ(mJ/mol K)	θ_D (K)	ρ_0 (μΩ·cm)	T_N (K)
bulk		1.4 (3.2)	610	n/a	311
0.75	350	2.3	392	6	300
0.75	20	1.9	478	16	>450
8	20	9.9	355	407	221

Antiferromagnetic CoO thin layers and nanoparticles

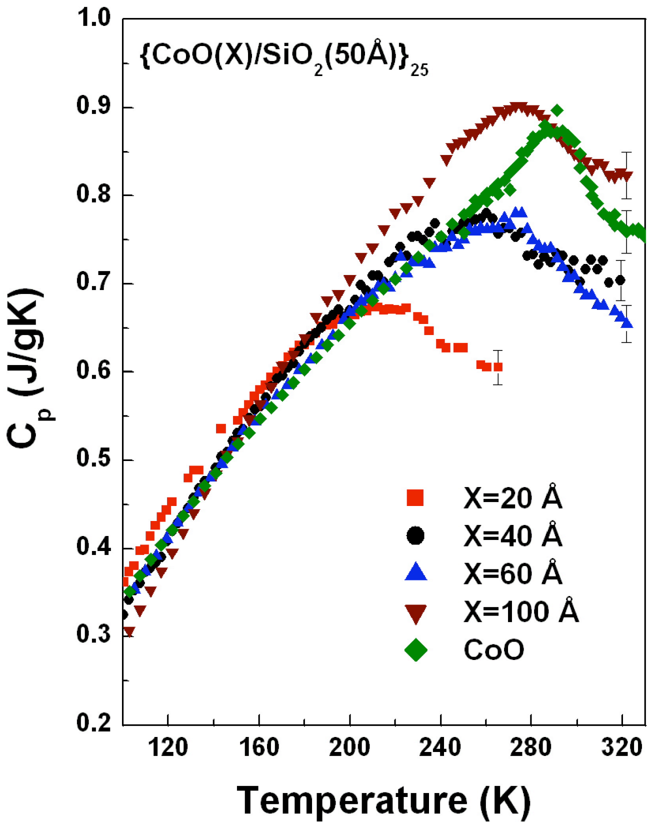
- 2D layers in multilayers
- 0D grains or particles (in matrix or granular)
- Study effects on Neel temperature, on magnons, phonons

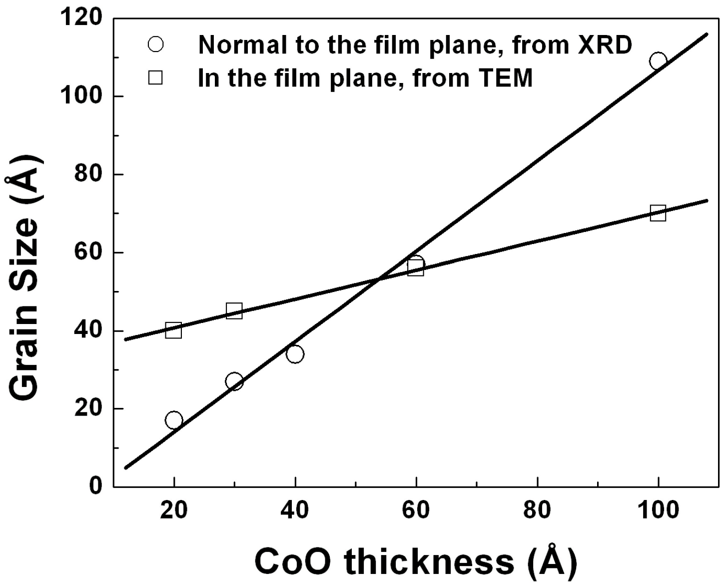
CoO/MgO multilayers:
very little suppression of T_N even at 1.6 nm



E. N. Abarra, K. Takano, F. Hellman, and A. E. Berkowitz, *Phys. Rev. Lett.* **77**, 3451 (1996).

CoO/a-SiO$_2$ multilayers





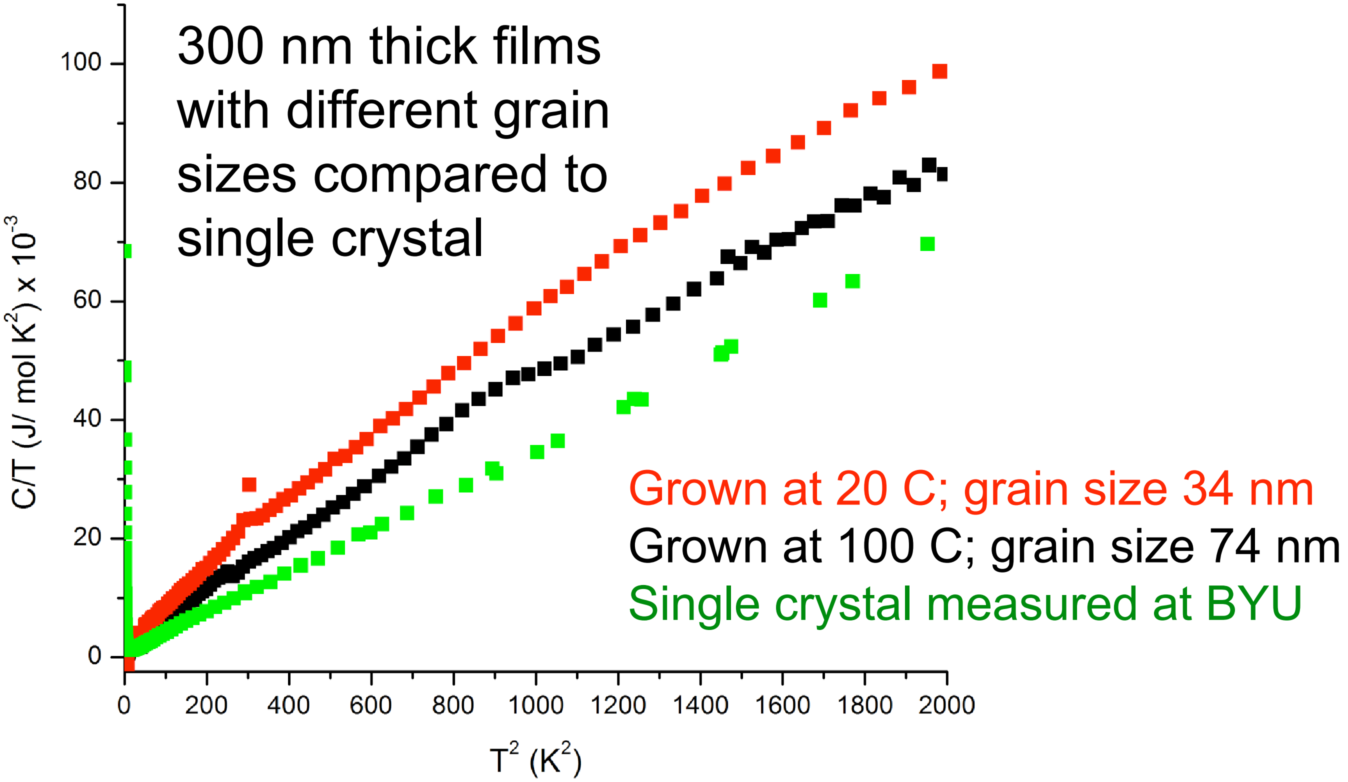
Y. J. Tang, D. J. Smith, B. L. Zink, F. Hellman, and A. E. Berkowitz, *Phys. Rev. B.* 67**, 054408 (2003).**

CoO layered with *a*-SiO$_2$: T_N strongly suppressed and broadened, unlike MgO

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 (preliminary results)

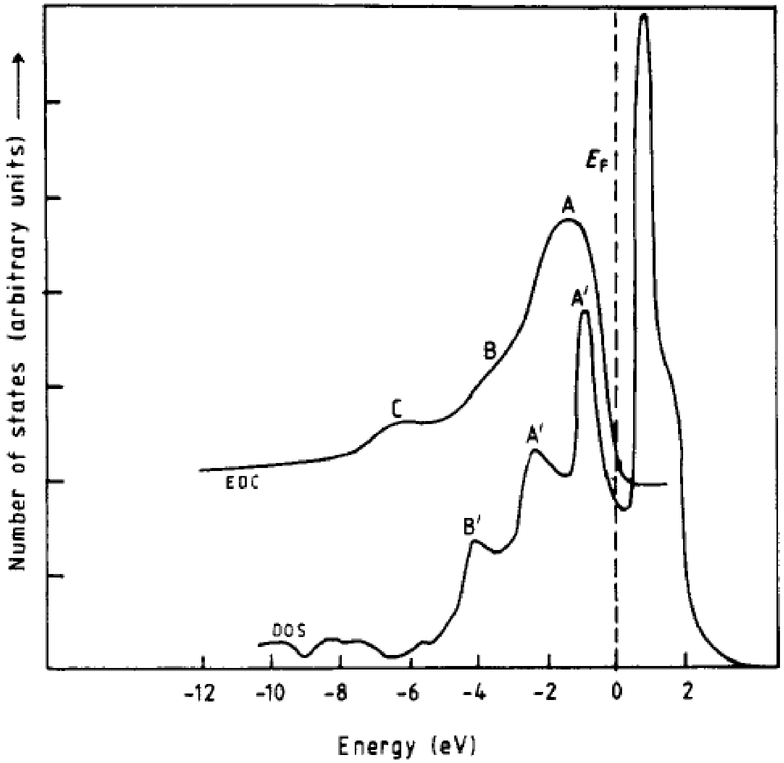


- Phonon softening at low temperature in samples with smaller grain size
- Small linear term also seen; likely due to disorder at grain boundaries
- Increased entropy: affects thermal stability of phases

Conclusions

1. Nanostructured materials have properties substantially different than bulk (examples: Cr, CoO).
    - Magnetic properties: length scales short for intrinsic properties like Curie temperature and anisotropy (few nm); longer (10’s of nm) for magnetic domain wall effects
    - Thermodynamic properties: expect similarly short length scale for intrinsic properties (e.g. electron, phonon, magnon DOS)
    - BUT, materials effects (e.g. water adsorption, surface segregation, structural disorder, strain) can be important at longer lengths (10’s - 100’s of nm)
2. Si-micromachined membrane based calorimetry devices used to measure C_p of films (and tiny crystals; μgrams) from 1-500K, 0-8T
    - Also used for measuring thermal conductivity, thermopower
    - Wide temperature, magnetic field range: entropy of nanoparticle systems
3. Low T: electron, phonon density of states
    - Fe/Cr giant magnetoresistance multilayers: enhanced electron density of states (2x Fe/Cr average), not dependent on field
    - Cr, CoO films show phonon softening: How common??
4. Magnetic transitions: ferromagnetic (FM), anti-FM, spin glass
    - Nanostructured CoO: Neel temperature suppressed, broadened

Cr band structure



- Band structure calculations
  - KKR method
  - Paramagnetic
- Fermi energy near a minimum in the DOS
- Broadening of the DOS will lead to enhanced values

N. C. Debnath et. al. J. Phys. F: Met. Phys. **15** (1985) 1693-1701