

Workshop on “Calorimetry-on-a Chip”; low temperature heat capacity measurements on microgram to milligram samples

Organized by Alexandra Navrotsky (UC Davis) and Frances Hellman (UC Berkeley)

Held at Annual COMPRES Meeting, June 16-19, 2005, Mohonk Mountain House, New Paltz NY

Workshop is Saturday June 18, 2005, 4-6 pm

The challenge and opportunity

Thermodynamic properties of high pressure phases continue to be important to deep earth problems; the focus is shifting increasingly to more complex and higher pressure materials relevant to the lower mantle, D' layer, and core. The effects of aluminum, iron, and other minor constituents on the thermodynamics of silicate spinel, perovskite, and post perovskite phases still are not well known. Magnetic and electronic transitions are not fully characterized.

Much of the difficulty arises from sample size: multianvil experiments produce milligrams of material, diamond anvil cells produce 1-100 micrograms. Though milligram-sized samples can be studied by oxide melt solution calorimetry [Navrotsky 1997, Ito 1990], smaller samples can not. Conventional adiabatic calorimetry to obtain heat capacities and standard entropies require grams of sample. Thus the entropies of high pressure materials, especially those which have structural and magnetic transitions, are not well known.

“Calorimetry-on-a-chip”, described below, provides heat capacity and phase transition data for films and small crystals in the microgram to milligram range. It has been applied, largely by the physics community, mainly to thin films, multilayers, and magnetic materials. This workshop is to explore its applications, potential, and limitations for high pressure materials of interest to the mineral physics community.

The goal of the workshop is to introduce “calorimetry on a chip” to the COMPRES community and to develop community interest in integrating such measurements into our technique base for high pressure materials. The first hour of the workshop will present the methodology (including showing some actual calorimetric detectors). The second hour will be general discussion. There will be refreshments appropriate to the hour.

Attendees at COMPRES are encouraged to participate. People in the mineralogy/petrology community who may not otherwise attend are encouraged to come for as much of the COMPRES meeting as possible. COMPRES will provide a “standard package” of support for local costs. Information on the COMPRES meeting is on the website <http://www.compres.stonybrook.edu/Meetings/2005-06-16-19/Index.html> For people coming only because they want to attend the workshop, some travel funding is available, contact Alex Navrotsky anavrotsky@ucdavis.edu

Frances Hellman is a condensed matter physicist at UC Berkeley who has collaborated with Alex Navrotsky for several years on nanophase thermodynamic problems. She looks forward to meeting the high pressure and mineral physics community.

The methodology is applicable to a wide variety of materials of interest to the broad mineral physics community. Projects, with different users, might include:

- (Mg,Fe) silicate spinels, including the effect of Fe^{3+}
- silicate perovskites, including substitution by iron and aluminum
- Fe_{1-x}O as a function of stoichiometry, including the high pressure almost stoichiometric material
- SiO_2 stishovite and selected high pressure hydrous magnesium silicates (alphabet phases), if this can be done accurately because of expected lower electrical and thermal conductivity
- High pressure phases in zirconia and titania
- Other quenchable phases from DAC experiments
- A general survey of magnetic transitions and other phase transitions in high pressure phases between 4 and 500 K.
- Cryogenically quenched high pressure phases, transferred directly into detector at low temperature, heat capacities and decomposition enthalpies, analogous to our previous work on $\text{Ca}(\text{OH})_2$ [Schoenitz 2000], but applicable to smaller samples
- High pressure sulfides and alloys of geophysical and planetary significance
- Materials relevant to the outer planets, gas clathrates, and other low T high P solids
- High pressure organic solids
- Measurement of thermal conductivity of high pressure materials may also be possible
- ***Whatever else people are interested in***

More Background and Technical Details

Short description of “calorimetry-on-a-chip”

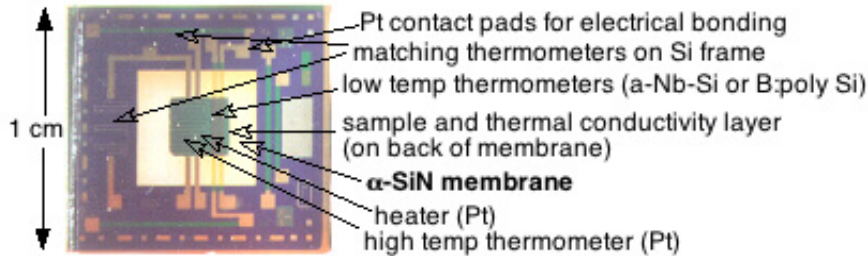
Specific heat measurements are based on a Si-micromachined calorimetry device which Hellman has spent many years developing [Denlinger 1994]. These calorimeters on a chip have been used for both thin films and small bulk samples. Different designs have been optimized for different uses, but the heart of the device is a thin (1800 Å) $0.5 \times 0.5 \text{ cm}^2$ amorphous Si_3N_4 membrane supported by a $1 \times 1 \text{ cm}^2$ Si frame. On one side of this membrane, we deposit and pattern thin film heater, thermometers, and electrical leads of appropriate resistance and temperature coefficient. On the other side, in a $0.25 \times 0.25 \text{ cm}^2$ area at the center, we deposit the sample and a thermally conducting material such as gold or copper. This thin membrane provides the necessary thermal isolation of sample from environment, while still providing a sample/thermometer platform. On the frame are matching thermometers to those on the membrane to permit a high sensitivity differential temperature measurement. A picture of the completed device is shown below. We have made thousands of these devices and have measured hundreds. The devices are metallurgically stable and physically robust under cycling between 4.2K and 1000K, and can withstand photolithographic processing. Because of the nature of the fabrication process, reproducibility of specific heat addenda and of thermal link between sample and environment is very good, varying from device to device by less than 5%. Samples are measured using the relaxation method, requiring a separate determination of the thermal link between sample and environment (the steady state increase of the sample temperature with the sample heater turned on) and the time constant of the relaxation of the sample temperature after turning off the sample heater. Further details about the devices and how they are measured can be found in [Denlinger 1994], [Zink 2002], [Zink 2004] and [Revaz 2003].

Using these devices we have measured thin film samples less than 1000 Å thick (weighing < 10 g) below 20K and 1000-5000 Å thick (weighing 10-50 g) up to 525K in magnetic fields from 0 to 8T to date to approximately 2% absolute accuracy (smaller samples can be measured with correspondingly less

accuracy when information such as an ordering temperature is desired). In most cases, the limit on accuracy is the uncertainty in the thickness of the thin film sample. Relative measurements such as at a phase transition are made with precision better than 1%. [Kim 2002b] We have also successfully measured small single crystal or other bulk samples (200-500 g) thermally anchored to the device by conducting grease, In, or Ga, and powder samples dissolved in a solvent and dropped onto devices.

Samples measured to date include amorphous magnetic films (*a*-TbFe₂ and giant negative magnetoresistance *a*-Gd-Si alloys) [Hellman 1998] [Zink 1999], empty and filled fullerenes (C₆₀, K₃C₆₀, C₈₂, La@C₈₂, C₈₄, and Sc₂@C₈₄) [Allen 1999a] [Allen 1999b], single crystal and pressed pellets of manganites and ruthenates [Kim 2002a], [Kim 2002b], [Kim 2003], magnetic and antiferromagnetic multilayered films (Fe/Cr; NiO/CoO, NiO/MgO, and CoO/MgO; CoO/SiO₂) [Revaz 2002], [Abarra 1996], [Tang 2003].

Figure 1 Picture of microcalorimeter (“calorimeter-on-a-chip”)



Example of work accomplished in a joint project involving Hellman and Navrotsky

As part of a DOE funded collaboration on nanomaterials, Navrotsky at Davis has been measuring heats of formation of nanophase cobalt oxides, Hellman at San Diego and Berkeley has been measuring heat capacities of CoO films by calorimetry-on-a-chip, and Boerio-Goates and Woodfield at BYU have measured heat capacities by adiabatic calorimetry using samples weighing several grams.

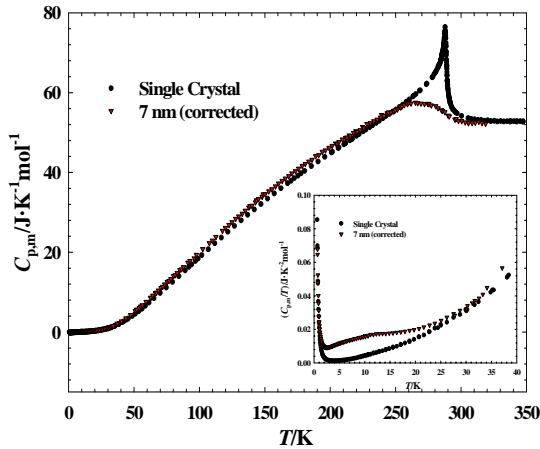


Figure 2 The heat capacity of 7 nm CoO corrected for water and Co₃O₄. ●, Single crystal CoO is included as a reference, ◆, Work at BYU.

CoO nanoparticles (7.0 ± 1 nm) were prepared by thermal decomposition of cobalt hydroxides in a hydrogen/argon atmosphere [Wang 2004]. Fig. 2 shows Cp of nano-CoO corrected for both water (as ice Ih) and Co₃O₄. Our results for single crystal CoO are shown for comparison. The inset shows the low temperature data, plotted as Cp/T vs. T, for both samples. A striking feature is the broadening of the magnetic transition in the nanoparticles. Using our Cp for CoO single crystal as a baseline, we calculated C_{excess} for nano-CoO. Below 250 K, C_{excess} is positive, but it turns negative at higher temperatures because of the larger magnetic anomaly in the single crystal. The excess entropy of the nanoparticle (S_{nano} – S_{crystal}) is positive at all temperatures. At 250 K, the excess entropy is about 2.4 J·K⁻¹·mol⁻¹ and it drops to 1.5 J·K⁻¹·mol⁻¹ at 298 K.

Assuming S_{excess} at 250 K arises primarily from surface contributions, we obtain a surface entropy of 2.8 mJ·K⁻¹·m⁻².

Fig. 3 shows low temperature Cp for films of CoO with different grain sizes, prepared by growing at different temperatures; data is plotted as Cp/T vs. T². These films weigh only a few micrograms and are measured using Si-micromachined calorimeters. As also seen in the 7 nm bulk sample of nanocomposite-

CoO, significant softening of the lattice (larger T^3 term and reduced Debye temperature) is seen in the film grown at room temperature compared to that grown at 100 °C; both films are softer than the bulk sample.

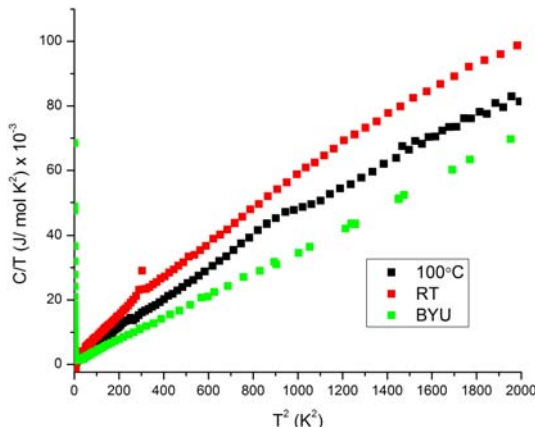


Figure 32 Low temperature C_p for 300 nm thick CoO films grown at 373 K (average grain size from XRD 74 nm) and room temperature (average grain size 34 nm) compared to single crystal data. The small bump near 900 K in one film reflects the antiferromagnetic ordering of a small amount of Co_3O_4 in this sample. Work at UCSD (films) and BYU (single crystal). Note Hellman has since moved from UCSD to UCB.

These studies and other work from Hellman's lab show that the delineation of heat capacities and phase transitions in very small samples at temperatures from liquid helium to about 500 °C is indeed feasible. Thus calorimetry-on-a-chip is compatible, in terms of sample size, with materials synthesized in and quenched from the multianvil press and diamond anvil cell. The accuracy on C_p depends on sample size and method used to attach the sample to the chip calorimeter. For thin films, we can achieve typically $\pm 2-5\%$. For bulk crystals, the current limit is a few hundred micrograms with an accuracy also of typically $\pm 2-5\%$, which is reduced as sample size drops. Using a redesigned chip, optimized for a bulk sample, the sample size limit can be lowered. To attach and thermally anchor the samples to the chips, Ga is likely to be the optimal choice as its heat capacity is reproducible and it does not require heating significantly above room temperature to achieve a good thermal contact. Equally importantly, phase transitions can be detected and their enthalpies measured. For high pressure samples available in microgram to milligram amounts, such transitions would include magnetic transitions, structural transitions, and decomposition upon heating. The enthalpy of the latter could be used to obtain the enthalpy of the high pressure phase relative to the decomposition product. If the decomposition product is a crystalline assemblage, larger quantities of it could be synthesized at atmospheric pressure and its enthalpy of formation determined by conventional oxide melt solution calorimetry in the Thermochemistry Facility at Davis [Navrotsky 1997]. If the product is amorphous, a corresponding synthetic glass could be dissolved (with some added uncertainty related to small differences between the materials produced by the two routes). Thus calorimetry-on-a-chip offers a potential route to the heat capacities, entropies, and enthalpies of formation of high pressure materials which can not be made in sufficient quantities for conventional measurements. To our knowledge this approach has not yet been applied to high pressure phases.

Specifically the following questions related to technique development for high pressure minerals need to be addressed.

- What limits are there on the samples in terms of electronic conductivity? For example, how much worse are heat capacity data across an Mg-Fe substituted series (e.g the olivines) $(Fe,Mg)_2SiO_4$ or magnesiowustites $(Mg,Fe)O$. In particular, can samples with geologically meaningful $Fe/(Fe+Mg)$ ratios (0.05 to 0.2) be measured? Of course, as the Mg?Fe ratio increases, the electrical conductivity and contributions to the heat capacity from electronic and magnetic transitions decrease, perhaps leading to less accurate C_p measurements.
- Can one obtain good heat capacity data for samples retrieved from multianvil or diamond cell experiments? Are there issues with sample size, thermal contact, crystal shape, etc.? What accuracy can one maintain in C_p ?
- Can one observe low T magnetic transitions in high P minerals? A test case might be Fe_2SiO_4 spinel?

Once this exploratory phase is completed with community participation, we anticipate a major COMPRES and/or NSF proposal to set up a calorimetry-on-a-chip facility for broad mineral physics use.

References:

- [Abarra 1996] E. N. Abarra, K. Takano, F. Hellman, and A. E. Berkowitz, "Thermodynamic measurements of magnetic ordering in antiferromagnetic superlattices", *Phys. Rev. Lett.* **77**, 3451 (1996).
- [Allen 1999a] K. Allen and F. Hellman, "Specific heat of endohedral and higher fullerene thin films", *Communications in J. Chem. Phys.* **111**, 5291 (1999).
- [Allen 1999b] K. Allen and F. Hellman "Specific heat of C₆₀ and K₃C₆₀ thin films, 6-400 K", *Phys. Rev. B* **60**, 11765 (1999).
- [Denlinger 1994] 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", *Rev. Sci. Instr.* **65**, 946 (1994).
- [Hellman 1998] F. Hellman, E. N. Abarra, A. L. Shapiro, and R. B. van Dover, "Specific Heat of Amorphous Rare Earth-Transition Metal Films", *Phys. Rev. B* **58**, 5672 (1998).
- [Ito 1990] E. Ito, M. Akaogi, L. Topor, and A. Navrotsky, Negative pressure-temperature slopes for reactions forming MgSiO₃ perovskite from calorimetry", *Science* **249**, 1275-1278 (1990).
- [Kim 2002a] D. Kim, F. Hellman, and J. M. D. Coey, Critical properties of La_{1-x}Sr_xMnO₃, *Phys. Rev. B* **65**, 214424 (2002).
- [Kim 2002b] D. Kim, B. Revaz, B. L. Zink, F. Hellman, J. F. Mitchell and J. J. Rhyne, Tricritical point and the doping dependence of the order of the ferromagnetic phase transition of La_{1-x}Ca_xMnO₃, *Phys. Rev. Lett.* **89**, 7202-06 (2002).
- [Kim 2003] D. Kim, B. L. Zink, F. Hellman, S. McCall, G. Cao, and J. E. Crow, Mean field behavior with Gaussian fluctuations at the ferromagnetic phase transition of SrRuO₃, *Phys. Rev. B Rapid Communications* **67**, 100406 (2003)
- [Navrotsky 1997] A. Navrotsky, Progress and new directions in high temperature calorimetry revisited, *Phys. Chem. Min.* **24**, 222-241 (1997).
- [Revaz 2003] B. Revaz, D. O'Neil, L. Hull, and F. Hellman, Numerical simulation of the heat transfer in a-Si-N-membrane based microcalorimeters, *Rev. Sci. Instr.* **74**, 4389 (2003).
- [Revaz 2002] B. Revaz, M.-C. Cyrille, B. Zink, I. K. Schuller and F. Hellman, "Enhancement of the electronic contribution to the low temperature specific heat of an Fe/Cr magnetic multilayer", *Phys. Rev. B* **65**, 944171 (2002).
- [Schoenitz 2000] M. Schoenitz, A. Navrotsky, and K. Leinenweber, The enthalpy of transformation of Ca(OH)₂-I (portlandite) to Ca(OH)₂-II (EuI₂ structure) by low-temperature DSC, *Phys. Chem. Min.* **27**, 604-609 (2000).
- [Tang 2003] Y. J. Tang, D. J. Smith, B. L. Zink, F. Hellman, and A. E. Berkowitz, Finite size effects on the moment and ordering temperatures in antiferromagnetic CoO layers, *Phys. Rev. B.* **67**, 054408 (2003).
- [Wang 2004] L. Wang, K. Vu, A. Navrotsky, R. Stevens, B.F. Woodfield, J. Boerio-Goates, Calorimetric study: of surface energetics and the magnetic transition in nanocrystalline CoO, *Chemistry of Materials* (in press).
- [Zink 1999] B. L. Zink, E. Janod, K. Allen, and F. Hellman, "Large Magnetic Entropy in Giant Negative Magnetoresistive Gd-Si", *Phys. Rev. Lett.* **83**, 2266 (1999).
- [Zink 2002] B. L. Zink, B. Revaz, R. Sappey, F. Hellman, Thin Film microcalorimeter for heat capacity measurements in high magnetic fields", *Rev. Sci. Instr.* **73**, 1841 (2002).
- [Zink 2004] B. L. Zink and F. Hellman, Specific heat and thermal conductivity of low-stress amorphous Si-N membranes", *Sol. St. Comm.* **129**, (2004).