In recent years we have participated in interdisciplinary projects studying materials that exhibit negative thermal expansion (they shrink when heated and expand when cooled), that are frustrated in their ability to order magnetically, or that form complex, open-framework networks useful for catalysis or separations of materials.

Currently, members of my research group are working on projects to study nanoparticles, particles with dimensions of a few nanometers. Given their size, such particles contain a relatively small number of molecular units, and they often have very different properties from those of the bulk material of the same chemical composition. An important question is to what extent the different behavior is due to the increased contributions of energetic surfaces because of the greater surface/volume ratio in nanoparticles and/or to differences on the interior of the particle associated with finite size effects.

There are some common elements to research projects in my laboratory, efforts which are shared with my BYU Colleague, Prof. Brian Woodfield and with a colleague at the University of California at Davis, Prof. Alexandra Navrotsky. These are illustrated in the figure on the right. Each project is very interdisciplinary, involving some mix of the traditional areas of physical, inorganic and analytical chemistry. Students who graduate from my laboratory have the opportunity to use a variety of synthetic techniques to prepare materials, to become skilled in cutting-edge analytical tools to characterize those materials, and to study those materials using thermophysical (heat capacity measurements from 0.6 to 800 K at BYU) and thermochemical (reaction calorimetry at Davis) techniques to probe the balance between entropic and energetic factors. Some details of our laboratory facilities are described at the link below. A good balance is also achieved with theory and experiment, because we often model our results with theoretical calculations. The actual mix of what happens in a specific project is tailored to the needs of a project and the interests of the student. In separate links below, we present summaries of two of our recent and on-going projects.

**Surface energies, entropies, and magnetic properties of Nano CoO**

CoO is of interest for both practical and theoretical reasons. It is used widely as the magnetic material on recording devices. While CoO has a simple face-centered cubic (NaCl) structure at room temperature in its paramagnetic phase, it undergoes a coupled structural-magnetic transition near 290 K into an antiferromagnetic monoclinic phase. The Co2+ ion is unusual in that the orbital angular momentum associated with the unpaired electrons is not fully quenched by the crystal field so that the magnetism is more complicated than it might be otherwise. There are also some indications that the bonding in CoO is primarily ionic rather than covalent and a claim has been made that the superexchange mechanism may not be operative here.

We have made heat capacity measurements on particles with diameters of \((7.0 \pm 1.0)\) nm. The nanoparticle \(C_p\) has a broad anomaly with a rounded maximum at 265 K, a reduction of 23 K from the
Néel temperature $T_N$ of single crystal CoO. The sharp peak that appears in single crystal CoO is indicative of long-range ordering of the magnetic spins. The rounding of the anomaly in the nanoparticles tells us that the long-range magnetic order is pretty much lost. The shape of the nanoparticle heat capacity and the location of $T_N$ is in excellent agreement with thin films of CoO of comparable dimensions.

From an analysis of the excess heat capacity, $C_{exc} = C(nano) - C(single\ crystal)$, we can calculate an excess entropy. The magnetic and surface contributions to the excess entropy cannot be resolved uniquely, but we can take the behavior of $C_{exc}$ in the region from 50 to 180 K as being typical of surfaces, and extrapolate that behavior through the transition region. From $S_{exc}$ = 245 and the surface area of the particle, we estimate the surface entropy as $(0.28 \pm 0.03)$ mJ K$^{-1}$ Am$^{-2}$ which is in line with the only literature report (for MgO). Then, depending on how we extrapolate $C_{exc}$ we get negative excess magnetic entropies that range from $(-1.7$ to $-0.8)$ J · K$^{-1}$ · mol$^{-1}$. The negative entropy supports the conclusion that long-range magnetic order is not established in the nanoparticles as compared to the single crystals.

**Analysis of the magnetic heat capacity in single crystal CoO**

The heat capacity is one of the few bulk physical properties amenable to theoretical modeling. The measured $C_p$ can be represented as the sum of various contributions depending upon the nature of the material under study. With data of an appropriate quality, one can obtain excellent fits of the theoretical models for these contributions. Our on-going work on single CoO illustrates this nicely. CoO is an interesting material because it has a magnetic transition at a temperature that is comparable to the temperatures needed to cause thermal excitation to excited crystal field states. Most magnetic materials order at temperatures that are much lower than the temperatures at which their excited electronic states become populated. The heat capacity of CoO can be considered to be a sum of three terms, the contributions from the lattice vibrations, the magnetic transition, and the electronic excitations. Getting at the magnetic contribution to the heat capacity is complicated by the need to eliminate the electronic (Schottky) contribution from the measured heat capacity as well as those of the lattice. The contributions of the lattice vibrations and the electronic excitations can be modeled if the vibrational and electronic energy levels are known from spectroscopic studies. The results of one attempt at such a modeling are shown in the figure below on the left, where the various contributions to $C_p$ are shown. To the right is the estimation of the magnetic contribution to the heat capacity. Because this estimation gives a magnetic entropy that is significantly higher than expected, we are trying other methods to estimate the lattice heat capacity, since this is the most likely culprit for the source of error.

**Laboratory Facilities**

**Calorimeters**

To get at entropies, we measure the heat capacity to temperatures as low as 0.6 K in one cryostat and have three others for work at higher temperatures. Three of the four are home-built calorimeters that have an accuracy and precision comparable to the best available in the world. The low-temperature semi-adiabatic apparatus operates from 0.5 # T/K # 100. In this region solid-state
phenomena such as magnetic transitions, superconductivity, charge and spin-density waves, take place. We have two calorimeters, one just developed, that cover the temperature range from 10 \( T/K \) \# 400. The high accuracy of this instrument up to 400 K allows accurate enthalpy increments and third-law entropies to be calculated. These apparati are used to study solid-state phenomena of interest (structural and magnetic phase transitions, for example) between 30 \( T/K \) \# 400. For higher temperature work, we have a Netsch differential scanning calorimeter (DSC) that is capable of measurements up to 800 K, on small samples (few mg) but with reduced accuracy and precision. In some problems, we combine results from all three types of calorimeters.

*Synthetic Facilities*

We have a variety of furnaces available for doing classical “beat and heat” synthesis and single crystal growth, and we can also do sol-gel and hydrothermal techniques for nanoparticle synthesis. Air and/or water sensitive samples are handled in a large Ar-filled glove box in which the water and oxygen contents are kept below 1 ppm.

*Sample Characterization Facilities*

BYU is well-equipped to do modern materials characterization. In 2004 alone, two new Transmission Electron Microscopes (TEM) and a new X-ray Diffractometer (XRD) capable of temperature dependent single crystal structure refinements were purchased. Our group makes use of thermogravimetry (TG), X-ray fluorescence (XRF), electron microprobe, photoelectron spectroscopy (PES), visible, infrared and Raman spectroscopies as appropriate for a particular problem. Brunauer-Emmet-Teller (BET) measurements for particle surface area measurements are usually done at U.C. Davis.