

FINAL REPORT: “Energetics of Nanomaterials”

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PI: Nancy Ross, Virginia Polytechnic Institute and State University

Associated Awards:

DE-FG02-05ER15667, PI: Alexandra Navrotsky, University of California, Davis

DE-FG02-05ER15666, PI: Brian Woodfield, Brigham Young University

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EXECUTIVE SUMMARY

Nanomaterials, solids with very small particle size, form the basis of new technologies that are revolutionizing fields such as energy, lighting, electronics, medical diagnostics, and drug delivery. These nanoparticles are different from conventional bulk materials in many ways we do not yet fully understand. This project focused on their structure and thermodynamics and emphasized the role of water in nanoparticle surfaces. Using a unique and synergistic combination of high-tech techniques—namely oxide melt solution calorimetry, cryogenic heat capacity measurements, and inelastic neutron scattering—this work has identified differences in structure, thermodynamic stability, and water behavior on nanoparticles as a function of composition and particle size. The systematics obtained increase the fundamental understanding needed to synthesize, retain, and apply these technologically important nanomaterials and to predict and tailor new materials for enhanced functionality, eventually leading to a more sustainable way of life.

COMPARISON OF ACTUAL ACCOMPLISHMENTS AND GOALS AND OBJECTIVES

We have followed the goals and plans of the proposals that have directed this project. We believe we have met and indeed exceeded the goals. There has been no major redirection of the project and the work has proven technically feasible. We have accomplished even more than we planned, as the extensive publications list shows.

PROJECT ACTIVITIES

Goals and Major Findings

Funded by the DOE Office of Science Separations program, the Navrotsky, Ross, and Woodfield groups have worked synergistically for over a decade to study the thermodynamics of nanoparticles and their surfaces; and the confinement of molecules, mainly H₂O, on surfaces and pores. The emphasis has been to develop a microscopic (atomistic) understanding of the basis of the complex thermodynamic behavior of high surface area materials by combining calorimetric measurements of heats of formation, heats of adsorption, and surface energies (Navrotsky); inelastic neutron scattering to probe structure and dynamics of water adsorbed on surfaces of nanoparticles (Ross); and entropies and low temperature physics via heat capacity measurements (Woodfield). Together, these combined methodologies have provided a unified picture of the lattice dynamics, stability, phase transitions, and the confinement of guest molecules of nanomaterials.

Our major conclusions, enabled by synergistic application of our different methodologies, are the following. There appears to be little excess heat capacity in nanoparticles related to lattice vibrations, but, because the particles are terminated by a water layer that cannot be removed completely, the adsorbed water contributes to the heat capacity and overall energetics. The energetics and lattice dynamics of the adsorbed water are complex, different from those of bulk liquid water or ice polymorphs, and are unique to different materials. Systematics, related more strongly to crystal structure than to composition, have been developed for the surface energies and water adsorption energies for many nanoparticulate systems. The interactions among

polymorphism, surface energies, and water adsorption cause significant changes in phase stability and phase diagrams—including for oxidation-reduction reactions--in nanoscale systems. Such changes affect processes using nanoparticles and high surface area materials, such as catalysis, sensing, and separations.

Individual Contributions and Synergies

Specifically we brought the following capabilities to bear on the joint projects.

Navrotsky: The Peter A. Rock Thermochemistry Laboratory and Navrotsky's group brought unique expertise in thermochemistry and the capability to measure enthalpies of formation of materials both by high temperature oxide melt solution calorimetry (for ceramic and zeolitic materials) and aqueous solution calorimetry (for hybrid materials), and measurement of guest-host interactions by gas adsorption calorimetry, liquid immersion calorimetry, and titration calorimetry. They also measure heat capacities and phase transition enthalpies above room temperature, as well as having considerable experience in materials synthesis and characterization.

Ross: The Ross group used high resolution, low temperature inelastic neutron scattering (INS) to determine the thermodynamic properties and dynamics of confined surface water species on metal-oxide nanoparticles. The methodology developed can be readily extended to the proposed study and provides a unique and powerful tool to explore the interactions of the guest molecules within the framework structures and the effect on their thermodynamic properties. The Ross group also brought expertise in studies of frameworks as a function of pressure and temperature using X-ray and neutron diffraction. Such studies are needed to reveal variations in local structure and dynamic behavior that give rise to the unusual physical properties of these novel materials, including phase transitions, negative thermal expansion, negative linear compressibility and pressure-induced amorphization.

Woodfield: The Woodfield group used low temperature heat capacity as the primary experimental tool to investigate the intrinsic properties of a wide variety of materials. In addition to integrating C_p and C_p/T to obtain the temperature dependence of the enthalpy and absolute entropy, respectively, the Woodfield group also developed powerful modeling capabilities that use low temperature heat capacity to reveal the roles of defects and vacancies and the gross features of the lattice density of states. This, combined with the INS work from the Ross group, provided a unique capability to determine the total and individual contributions of lattice changes and guest-host interactions to the lattice dynamics and confinement.

Our various collaborations have led to over 40 joint papers in the past 15 years. Here we list a selection to show the breadth of our joint efforts

Specific Highlights

Surface Energies, Thermochemistry of Nanoparticles, and Changes in Stability at the Nanoscale

Since the late 1990s, nanomaterials and nanotechnology have become almost household words, and a huge volume of research, mainly on their synthesis and properties, has emerged. Despite this interest, knowledge of the energetic driving forces which make nanomaterials different from bulk materials remained poorly understood. High temperature oxide melt solution calorimetry in combination with room temperature water adsorption calorimetry provided a breakthrough in experimental determination of nanophase thermodynamics. Briefly the issues

are the following. Nanoparticles are higher in energy (enthalpy, free energy) than bulk materials because of the significant positive surface energy associated with their high surface area. Thus in principle, measuring the enthalpy of drop solution of samples with different surface areas should give a linear dependence, with the slope giving the surface energy. This simple picture is complicated by several factors. (1) Nanoparticles are generally strongly hydrated and not all the chemisorbed water can be removed without coarsening the particles. (2) The particles usually are not monodisperse and show a variety of exposed surfaces, so the energy measured is an average over the distribution of sizes and facets in the real particle rather than that of a specific crystallographic surface. This is a disadvantage in comparing experimental and theoretical surface energies but a potential advantage in providing useful values for “real world” nanomaterials. (3) The particles are often aggregated or agglomerated, so interfaces (grain boundaries) as well as external surfaces must be considered. The past decade has seen extensive effort as part of this project to address these issues, develop a systematic set of energetic parameters for nanoparticles, and apply such systematics to understanding nanoparticle behavior and properties

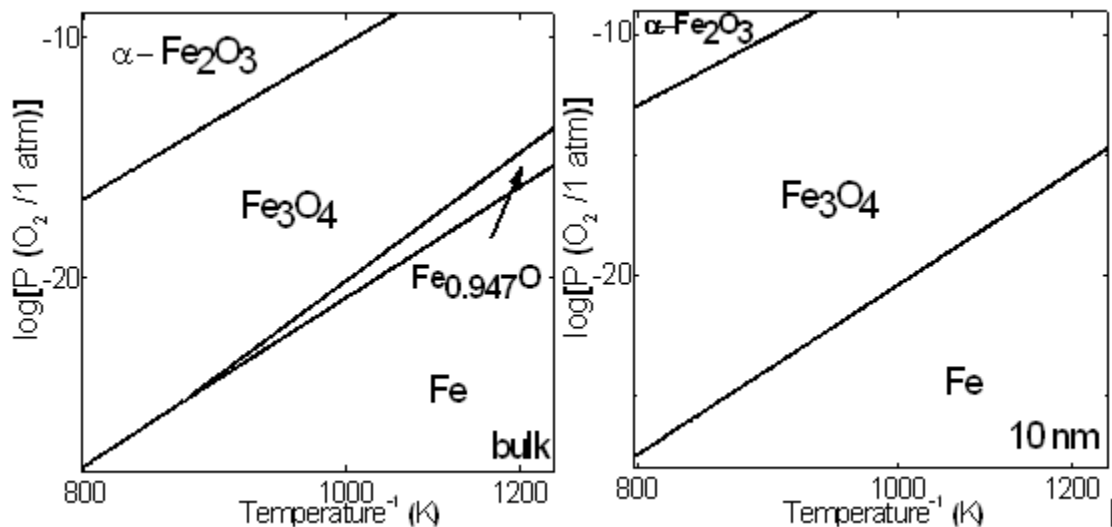
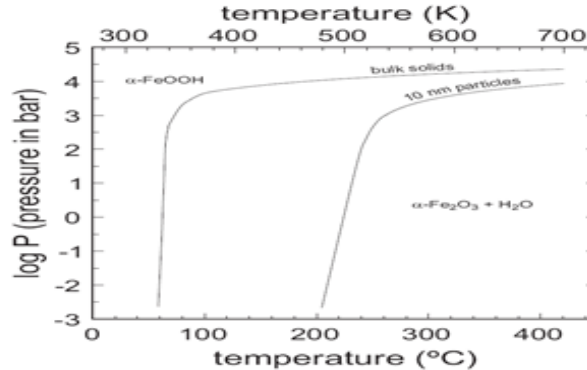
We have measured surface enthalpies of a large number of oxides in this project, enabling systematics to be developed. Several points stand out. (1) Surface energies are in the range 0.5 to 4 J/m², with many in the range 1 - 2 J/m². (2) The surface energy of different polymorphs can be significantly different as can that of particles with different morphologies. (3) Materials with spinel structure generally have fairly low surface energies. (4) Oxyhydroxides have lower surface energies than their corresponding anhydrous oxide phases. (5) The energy of the hydrated surface is smaller than that of the anhydrous, reflecting the exothermic enthalpy of hydration. The enthalpy of water adsorption (hydration) generally scales with the surface energy, higher energy surfaces hydrate more exothermically. (6) The measured surface energies are usually in reasonable agreement with those calculated by density functional theory. The measured energies often lie within the range of those computed for the two or three lowest energy surfaces, perhaps reflecting the complexity of the nanoparticle morphology.

These observations above lead to some general consequences for phase stability at the nanoscale. (1) The differences in surface energy between polymorphs result in crossovers in the thermodynamic stability of polymorphs at the nanoscale (McHale et al. 1997, Ranade et al. 2002, Levchenko et al. 2006, Navrotsky et al. 2008). Although all nanoparticles are higher in energy, enthalpy, and free energy than their bulk counterparts, in many systems, especially at temperatures below 200 - 400 °C, coarsening does not occur and the particle size distribution remains that obtained in the original synthesis. Under that constraint the system can minimize its free energy by transforming to a polymorph of lower surface energy. (2) Small particle size thermodynamically favors oxyhydroxides over oxides, leading to an increase of equilibrium dehydration temperature of as much as 100 °C (Navrotsky et al. 2008). (3) Particle size also affects oxidation-reduction equilibria (Navrotsky et al. 2010, Birkner and Navrotsky 2012) because the reduced and oxidized phases have different surface energies. Because the spinels Mn₃O₄, Fe₃O₄ and Co₃O₄ have lower surface energy than their competing phases, their stability fields in oxygen fugacity – temperature space is expanded at the nanoscale. The figure below shows the size-induced shifts in polymorphism, dehydration, and redox reactions for some oxides in the iron – oxygen system.

These changes in stability at the nanoscale have implications for geochemical and technological processes. Most importantly, one cannot simply use thermodynamic data for bulk phases to calculate equilibria at the nanoscale. Inasmuch as different phases have different

catalytic, biological, and environmental characteristics, what phase is actually present can have major consequences on both natural and technological processes.

Goethite = Hematite + Water



Heat Capacity Models and the Gapped Phonon Spectrum

The heat capacity is a measure of all the occupied energy states (such as vibrational, electronic, and magnetic) of a material at a given temperature, and the temperature dependence of each contribution can be modeled using theoretical functions. For instance, all solids exhibit a Debye dependence from phonons that, at low temperatures, approximates to odd powers in T beginning with the well-known T^3 term. Ferromagnetic and antiferromagnetic materials have $T^{3/2}$ and T^3 dependences, respectively. Other magnetic contributions may have gapped ferromagnetic ($T^{3/2}e^{-\delta/T}$) or antiferromagnetic ($T^2e^{-\delta/T}$) terms due to anisotropy, and a nuclear hyperfine contribution can be modeled with T^{-2} . Perhaps the most common non-phonon contribution to the low T specific heat is the linear term, $C_{lin} = \gamma T$, which was originally observed for free electrons in metals but more recently has also been attributed to other non-metallic properties. Since the heat capacity is a bulk measurement, the fitting of the low temperature heat capacity data to these

theoretical functions allows us to extract the intrinsic properties of a material in addition to calculating the absolute entropy.

We have repeatedly encountered nanomaterials and framework materials for which the standard heat capacity fitting expressions are no longer valid to within the experimental uncertainties. We have found that a linear term (traditionally associated with conduction electrons) is required for most insulating oxide nanomaterials and Debye functions are no longer sufficient to represent the lattice for framework materials such as zeolites; and we have developed new physical models that explain this behavior. The need for linear terms is linked to vacancies or other defects in the lattice, which is most pronounced in high surface area materials. The linear term is a direct measure of the oxygen vacancy or defect concentration. For framework materials, we have found that the phonon density of states does not go to zero as ν^2 , as is required for the Debye function, but instead drops abruptly to zero in the low energy regime. We can model this behavior in the Debye low temperature limit by introducing a gap term similar to what is used for anisotropic magnon behavior.

Control of Pore Structure, Acid Sites, and Thermal Stability in Synthetic γ -Aluminas

Mesoporous γ -alumina is the most extensively used catalyst support in a wide range of catalytic processes because of its favorable combination of physical, textural, thermal, and chemical properties. Control of the pore properties is highly valued since high surface area and large pore volume enable higher loading of active catalytic phases, while design of pore size and pore size distribution is critical to optimize pore diffusional transport and product selectivity. In addition to pore structure, its thermal and hydrothermal stability is also vital, since high temperature and/or steam-induced sintering causes serious reduction of surface area and pore volume resulting in the deactivation of the active catalytic phase.

The Woodfield group continues to develop synthetic techniques that provide control over pore properties, chemistry, and thermal stability that, in turn, can be investigated using calorimetric and structural techniques. One of our important outcomes is the development of simple, one-step methodologies to synthesize mesoporous γ -alumina with control of pore diameters (3 nm to 45 nm), high surface areas ($> 350 \text{ m}^2/\text{g}$), pore volumes (0.6 to $1.6 \text{ cm}^3/\text{g}$); thermal stability of the γ phase up to 1200°C for 24 hours in steam; the ability to mill the aluminas down to 50 nm sizes within 15 minutes; and control of Lewis and Brønsted acid site concentration (from 600 to $0 \text{ }\mu\text{mol/g}$) and of acid strength inside the pores. This type of control for aluminas is unprecedented, and we have several ongoing studies on these materials.

The Lattice Contribution is the Same for Bulk and Nanomaterials

Based on rather scattered studies of metals, alloys and a few binary oxides, it was concluded, mainly in informal discussions in the scientific community, that the heat capacity of nanoparticles is higher than that of the bulk. This supports intuition that atoms near the surface are bound less tightly. We have measured the heat capacity of a set of TiO_2 anatase and rutile nanoparticles and bulk materials. By successively reducing the water content without changing particle size, and measuring the water content and the heat capacity, we could separate the effects of water from those of particle size. In contrast to the prevailing belief that nanoparticles have higher heat capacities, we observed that heat capacities of anatase and rutile nanoparticles in the low temperature range 15 - 350 K are not significantly different from those of the bulk, when proper corrections for water are made. The apparently higher heat capacities for nanoparticle oxides suggested earlier probably arise from the lack of a correction for water.

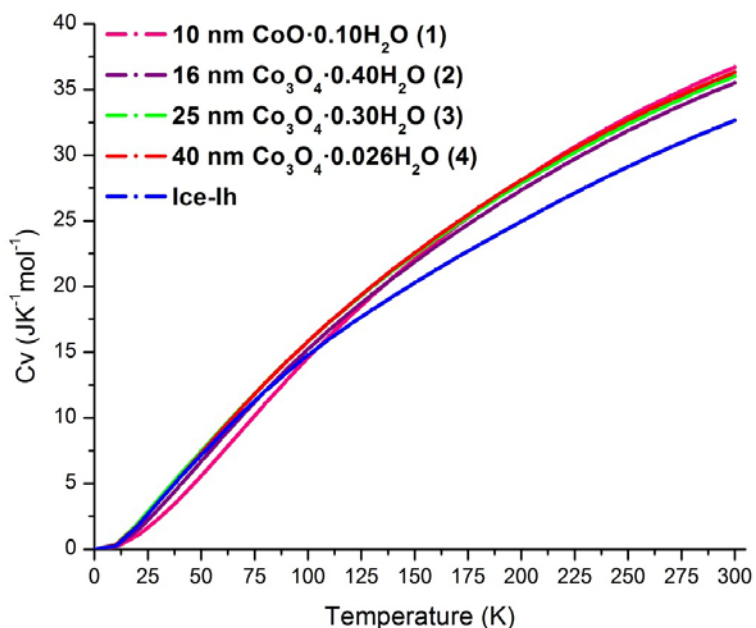
Since water has a lower molecular weight than most oxides, a gram of wet sample contains more oscillators than a gram of dry, leading to a seemingly larger molar heat capacity regardless of the details of the vibrations. Thus the proper correction for water is the leading term in correcting for the heat capacity of the nanoparticles. Therefore the intuition that nanoparticles have higher heat capacities than bulk materials is wrong, at least for titania down to a particle size of 7 nm. Similar measurements were performed on SnO₂ with similar results.

Our work also addresses the heat capacity of the adsorbed water in more detail. We have shown that, reflecting strong interaction of water with the TiO₂ surface, as already seen in the H₂O vapor adsorption calorimetry, the heat capacity and entropy of surface-confined water is somewhat smaller than that of bulk ice. This might be surprising at first glance if one expects higher heat capacities and entropies of water due to disordering and/or mobility at the interface. However, the tight bonding of the surface water appears to dominate the energetics.

Inelastic Neutron Scattering Studies of Water on Nanoparticle Surfaces

Navrotsky and Woodfield have shown that surface water is of critical importance in nanomaterial science as it affects the stability of metal oxide nanoparticles. Inelastic neutron scattering (INS) provides the ideal method to study the molecular vibrations of water adsorbed onto the surface of oxide nanoparticles as neutrons are highly sensitive to scattering by hydrogen atoms and much less sensitive to scattering from the metal oxides. These experiments not only provide information about the structure and dynamics of water confined on the surfaces of oxide nanoparticles, but they also allow one to calculate the heat capacities and entropies of the hydration layers from the vibrational density of states (VDOS) determined by the INS experiments. The calculated heat capacities can be compared with those measured by low temperature adiabatic calorimetry, thus providing an atomic scale understanding about the energetic and stabilities of nanoparticles.

INS has been employed to assess the structure and dynamics of the hydration layers of numerous metal oxide nanoparticle systems including TiO₂ (rutile and anatase), SnO₂ (cassiterite), CoO and Co₃O₄, CeO₂, CuO, ZnO, PdO, γ -Al₂O₃, Fe₂O₃, Fe₃O₄ and CuO. All of these studies support the finding that surface water achieves a multilayer structure upon the particle surface; the first water layer comprises a combination of chemically bound hydroxyl (OH) groups, generated by the dissociation of molecular water upon interaction with the metal oxide surface, and chemisorbed H₂O molecules. Subsequent layers are typically composed of water molecules hydrogen bonded to the first water layer and neighboring H₂O molecules. The ratio of molecular to dissociated water species is a consequence of the physical and structural properties of the exposed metal oxide surface.



We have also used results from the INS spectra to develop the vibrational density of states (VDOS) from which we are able to calculate the thermodynamic properties of the hydration layers confined to the surface of metal oxide nanoparticles. An example of the calculated heat capacities for Co-oxides is shown to the right.

INS analysis also allows in-depth appraisal of the thermodynamic properties of magnetic nanoparticles - no other analytical technique has the capability of providing such comprehensive information. For example, an INS spectrum for hydrated Co_3O_4 nanoparticles was collected at 11 K and showed a well-defined peak at 5 meV that was attributed to the magnetic excitation of the antiferromagnetic particles. Furthermore, its position in the spectrum was shown to be independent of the particle size. The exact origin of this magnetic spinwave is complex, but the electronic environments and spin-orbit coupling between the $\text{Co}^{3+}/\text{Co}^{2+}$ ions is liable to have an effect on the physical nature of its excitation. The magnetic contribution to the heat capacity (C_m) of the Co_3O_4 particles was calculated from the peak energy.

The thermodynamic properties of hydrated $\alpha\text{-Fe}_2\text{O}_3$ (hematite) and Fe_3O_4 (magnetite) nanoparticles have also been evaluated by INS methods. We have determined, for the first time, the contribution of the two-level magnetic spin flip transition to the heat capacity of the $\alpha\text{-Fe}_2\text{O}_3$ particles. In addition, the isochoric heat capacity of the water confined on the surface of these two types of iron oxide particles have been calculated from their INS spectra and is affected by the chemical composition of the underlying particle. Furthermore, the heat capacity and dynamics of the particle hydration layers appear to be influenced by a complex array of factors including particle size, water coverage and possibly the magnetic state of the particle itself.

Analysis of the magnetic properties of copper oxide (CuO) are underway. Bulk CuO undergoes two magnetic phase transitions: above T_N of ca. 230K, an antiferromagnetic ordering of the spins is maintained, but the remaining spins are disordered in a paramagnetic manner. Below T_N , a 3D incommensurate state is created in which spins are ordered in a helical arrangement. The INS data being analyzed will allow us to assess the effect of particle size on the magnetic behaviour of CuO which appears to be unique.

PRODUCTS

Complete Publication List for DEFG0205ER15666 (BYU), DEFG0205ER15667 (UCD), DEFG0205ER15668 (VT)

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Patents

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Techniques and Equipment

Navrotsky's group have advanced techniques in oxide melt solution calorimetry and gas adsorption calorimetry. In addition, the Calvet microcalorimeter used for oxide melt solution calorimetry has been commercialized as the AlexSYS, sold by Setaram, Inc. Cailures France. Instruments are now operational at Notre Dame University, Los Alamos National Lab, Pacific Northwest National Lab, and Clemson University, as well as in Europe and Asia

Websites and Other Electronic Media

The Principal Investigator, Alexandra Navrotsky is the Director of NEAT ORU (Nanomaterials in the Environment, Agriculture and Technology Organized Research Unit) and the Peter A. Rock Thermochemistry Laboratory. The overall research studies of both of these entities focus on nanomaterials and thermodynamic studies. The websites for both of these entities discuss the overall research of NEAT: <http://neat.ucdavis.edu/> and the Peter A. Rock Thermochemistry Laboratory: <http://thermo.ucdavis.edu/>

A video about the overall research and goals of NEAT:
<https://www.youtube.com/watch?v=F7f0MjvcVqc>