

Size-induced Shifts in Oxidation-Reduction Phase Equilibria in Nanophase Transition Metal Oxides



Pacific Northwest
NATIONAL LABORATORY

Proudly Operated by **Battelle** Since 1965

Frontiers in Geochemistry
Seminar Series

Presented by...

Professor Alexandra Navrotsky

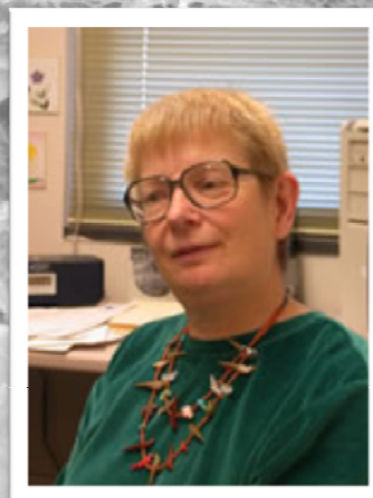
- Director, NEAT ORU
- Edward Roessler Chair in Mathematical and Physical Sciences
- Distinguished Professor, Interdisciplinary Professor of Ceramic, Earth, and Environmental Materials Chemistry at the University of California at Davis

It is now well established that differences in surface energies can alter the relative free energies of different polymorphs, causing size driven thermodynamic crossovers in phase stability at the nanoscale. It has also been shown that, because oxyhydroxides generally have smaller surface energies than oxides, dehydration equilibria, e.g. goethite to hematite plus water, can shift to higher temperature by as much as 100 K at the nanoscale. A general formulation of the effect of particle size on chemical equilibria among solid phases is that increasing surface area will favor the phase assemblage of lower surface energy.

There is now new thermochemical evidence for strong thermodynamic shifts in the position of oxidation-reduction (redox) equilibria in oxides at the nanoscale. Using new calorimetric data on surface energies in the cobalt-oxygen system, we show that the thermodynamic phase field in oxygen fugacity-temperature space of the divalent rocksalt oxide CoO is substantially narrowed at the nanoscale, bringing the reduction to Co metal to higher oxygen fugacity and the oxidation to Co_3O_4 spinel to lower oxygen fugacity at a given temperature. Metals generally have lower surface energy than oxides and we present evidence that spinels have lower surface energy than rocksalt oxides. Thus the contraction of the stability field of the divalent oxide, MO, relative to the metal, M, and the spinel M_3O_4 , is probably a general phenomenon. In the iron-oxygen system, wustite, Fe_{1-x}O , is thermodynamically unstable with respect to iron and magnetite, Fe_3O_4 , below the melting point of bulk wustite (1650 K) for particle sizes below 16 nm, in contrast to being stable above 850 K for the bulk. These size-driven redox changes have implications for material preparation and characterization, catalysis and the splitting of water in the presence of transition metal oxide nanoparticles, as well as for environmental, geological, and biological redox reactions.

More info:

Dr. Kevin Rosso, 371-6357



Tuesday

May 18, 2010

EMSL Auditorium

9:00 – 10:00 am