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Size-induced Shifts in the Thermodynamics of Nanophase Oxides and Implications for Materials Science, Geochemistry and Environmental Sciences

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It is well established that difference 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 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 Co₃O₄ 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 M₃O₄, is probably a general phenomenon. In the iron-oxygen system, wustite, Fe_{1-x}O, is thermodynamically unstable with respect to iron and magnetite, Fe₃O₄, 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. It is important to realize that the effects discussed here are thermodynamic in nature, and these thermodynamic driving forces set the stage for differences in kinetics and chemical reactivity at the nanoscale. Similar effects are seen in manganese oxides, and their shifts in redox equilibria and hydration state are linked in a complex manner.

Studies of stability and surface energy of materials useful for solid oxide fuel cells, batteries, and sensors suggest that low surface energy leads to easier displacement of surface water by other molecules and better transport of ions through the surface and between the solid and solution phases. Nanoparticles are ubiquitous in the environment, where initially formed fine grained precipitates coarsen only very slowly. These size-driven phase stability 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. These changes can affect the transport, solubility and bioavailability of heavy metals in the environment. A further complication is the formation of nanoscale clusters (polyoxometallates) for metals ranging from aluminium to uranium.

Alexandra Navrotsky was educated at the University of Chicago (B.S., M.S., and Ph.D. in physical chemistry). After postdoctoral work in Germany and at Penn State University, she joined the faculty in Chemistry at Arizona State University, where she remained till her move to the Department of Geological and Geophysical Sciences at Princeton University in 1985. She chaired that department from 1988 to 1991 and has been active in the Princeton Materials Institute. In 1997, she became an Interdisciplinary Professor of Ceramic, Earth, and Environmental Materials Chemistry at the University of California at Davis and was appointed Edward Roessler Chair in Mathematical and Physical Sciences in 2001.

Her research interests have centered about relating microscopic features of structure and bonding to macroscopic thermodynamic behavior in minerals, ceramics, and other complex materials. She has made contributions to mineral thermodynamics; mantle mineralogy and high pressure phase transitions; silicate melt and glass thermodynamics; order-disorder in spinels; framework silicates; and other oxides; ceramic processing; oxide superconductors; nanophase oxides, zeolites, nitrides, perovskites; and the general problem of structure-energy-property systematics. The main technical area of her laboratory is high temperature reaction calorimetry. She is director of the UC Davis Organized Research Unit on Nanomaterials in the Environment, Agriculture and Technology (NEAT-ORU). She has published over 700 scientific papers.

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