

Ram Seshadri MRL 2031, x6129 seshadri@mrl.ucsb.edu <http://www.mrl.ucsb.edu/~seshadri/teach.html>

An Overview of Some Advanced Inorganic Materials

In this self-contained course, we will attempt to understand inorganic materials from a microscopic/atomic viewpoint — how they form, their structures, bonding, electronic structures. . . and how these manifest in material properties. At every point, the emphasis shall be on why a particular material is possessed of a specific (set of) property(ies).

The material properties discussed in this course are those associated with the unit cell (perfect single crystals). In general, we will not consider the strengths of real materials as these are properties requiring insights beyond the unit cell.

This first class is about three representative advanced materials of current interest.

Negative thermal expansion in ZrW_2O_8

The cubic compound ZrW_2O_8 shrinks in volume upon being heated between 0.3 K and 1050 K. At 1050 K, it decomposes [Mary, Evans, Vogt and Sleight, *Science*, **272** (1996) 90]. To understand this unusual behavior, one must first understand thermal expansion.

To a good approximation, the potential energy $V(r)$ of interaction between neighboring atoms in a solid, as a function of the inter-atom separation r can be described by a curve that looks like the accompanying figure.

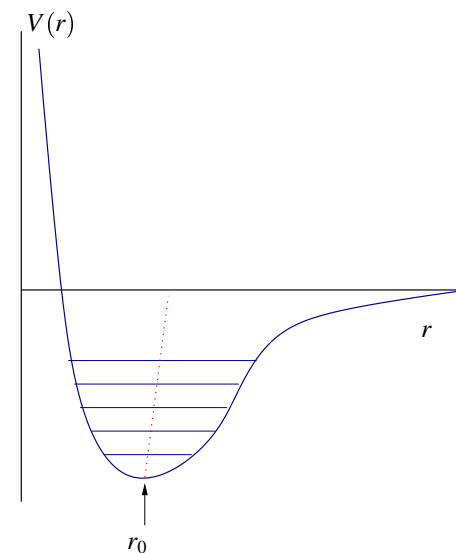
The horizontal lines represent vibrational energy levels. At very low temperatures, only the bottommost level is populated and the most stable distance is $r = r_0$. As the temperature is raised, the higher vibrational levels are populated and the equilibrium distance shifts slightly, so that it remains in the middle of the $V(r)$ vs. r trace, where it has maximum probability. This results in expansion of the material (since the equilibrium distance is increased). Note that such expansion would not take place were the $V(r)$ vs. r trace *harmonic* (symmetric across the middle).

This description, while effective for simple crystals and for linear chains *etc.*, fails in many cases. For example, polymer chains (rubber bands) often display negative thermal expansion — a rubber band contracts upon heating. Simple models of polymer chains based on self-avoiding walks (See H. B. Callen, *Thermodynamics and an Introduction to Thermostatistics*) explain such behavior on the basis of the entropy of a rubber band. A stretched polymer chain is in a low entropy state (very few configurations to explore) whilst a contracted polymer chain has many more configurations Ω and therefore higher entropy $S = k_B \ln \Omega$. As the temperature is raised, the higher entropy (more contracted) state is more favored. It is assumed that the energy does not change very much with change in configuration (or temperature).

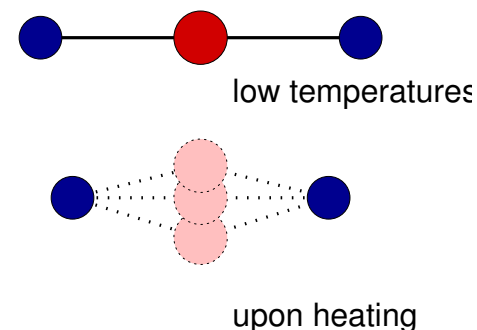
Some inorganic solids contract upon heating. A good example is ice- I_h , which over a small temperature range, contracts (and as does liquid water between 0 and 4°C). Many of the solids which do contract share a feature with ice- I_h , namely of tetrahedral coordination of certain ions.

In some solids (such as ones showing negative thermal expansion) the M-O-M framework can, upon heating, respond through transverse vibrations of the central ion (oxygen). If the M-O expansion is small and the amplitude of transverse vibrations are large, an effective bond contraction can result.

The compound ZrW_2O_8 , prepared and studied by Sleight and coworkers, has rigid ZrO_6 octahedra linked together by rigid WO_6 tetrahedra. Because Zr^{4+} and W^{6+} are highly charged and the coordination numbers in octahedra and tetrahedra are small (6 and 4) there is almost no change in the Zr-O or W-O bond length upon heating. Oxygen



Typical interaction potential between neighbors in a solid



Transverse vibrations = lattice contraction

atoms linking the polyhedra however, are permitted a wide range of M-O-M angles. Transverse vibrations of O therefore result in negative thermal expansion. The structure of ZrW_2O_8 is sketched below, with dark green ZrO_6 octahedra linked through yellow WO_4 tetrahedra.

Superconductivity in a layered cobalt oxide

In 1986, Bednorz and Müller published their famous discovery of high temperature superconductivity in a layered copper oxide. [J. G. Bednorz and K. A. Müller, Possible high- T_C superconductivity in the Ba-La-Cu-O system, *Z. Phys B* **64** (1986) 189-193.]¹ Prior to 1986, no oxide material had displayed a superconducting transition temperature exceeding 12 K. Within a year of the Bednorz-Müller paper, superconducting transition temperatures in related layered copper oxides had crossed the magical 77 K threshold (the boiling point of liquid nitrogen). Attempts to obtain superconducting compounds based on layered oxides other than those of copper have not met with much success. Notable exceptions include a report by Stacy and coworkers on superconductivity in layered niobium oxides [M. J. Geselbracht, T. J. Richardson and A. M. Stacy, Superconductivity in the layered compound, Li_xNbO_2 , *Nature* **35** (1990) 345.] and by Maeno, Bednorz and coworkers on the layered ruthenium oxide Sr_2RuO_4 [Y. Maeno, H. Hashimoto, K. Yoshida, S. Nishizaki, T. Fujita, J.G. Bednorz and F. Lichtenberg, Superconductivity in a layered perovskite without copper, *Nature* **372** (1994) 532.] In 2003, there has been some excitement about a layered cobalt oxide superconductor [K. Takada, H. Sakurai, E. Takayama-Muromachi, R. A. Dilanian and T. Sasaki, Superconductivity in two-dimensional CoO_2 layers, *Nature* **422** (2003) 53.] Note that all of these non-copper oxide compounds have rather low superconducting transition temperatures (below 10 K in all cases).

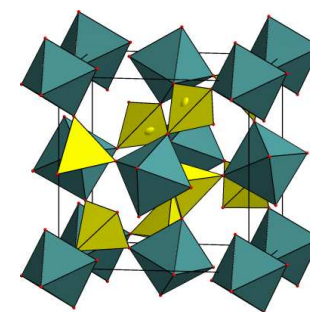
Na_xCoO_2 ($x \leq 1$) is a layered cobalt oxide bronze (so called because of the striking colors related compounds display). The compound $\text{Na}_{0.7}\text{CoO}_2$ was prepared by heating Na_2CO_3 and Co_3O_4 (taken in suitable proportions) in oxygen at 800°C for 8 h. This compound was then treated in an excess of Br_2 in acetonitrile solvent. Elemental bromine is an oxidizing agent. Here it oxidizes Co, and concurrently removes Na^+ from the lattice. Such Na^+ removal is favored by the high heat of formation of NaBr . The process also introduces water into the interlayer region (shown in the figure). Such water *intercalation* results in a significant lattice expansion. The authors determine their product composition to be $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ with ($x = 0.3$ and $y = 1.3$).

It is interesting that a cobalt compound is superconducting at all. Cobalt has 7 d electrons, and the metal as well as many Co compounds are magnetic. Magnetism and superconductivity are usually mutually incompatible. The unusual low-spin state of Co in this compound (octahedral, low-spin, $d^{5.3}$) is an important consideration for superconductivity.

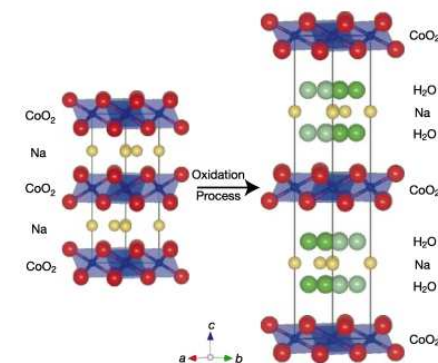
Recently, Cava and coworkers [R. E. Schaak, T. Klimczuk, M. L. Foo and R. J. Cava, Superconductivity phase diagram of $\text{Na}_x\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$, *Nature* **424** (2003) 527] have recently mapped out the T_C vs. composition phase diagram of $\text{Na}_x\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ and shown that these compounds resemble the superconducting copper oxides in that the T_C goes through a maximum corresponding to an optimum x value (an optimum oxidation state of Co).

Another interesting aspect is that water is driven off from the crystal at temperatures as low as 30°C , and the “dry” compound is no longer expected to superconduct.

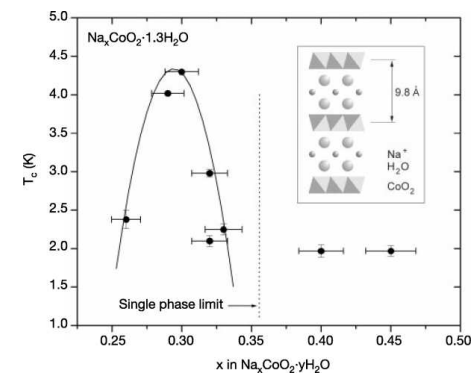
¹The impact of this paper can be judged by the over 6500 citations it has collected.



ZrW_2O_8



Oxidative water intercalation in Na_xCoO_2



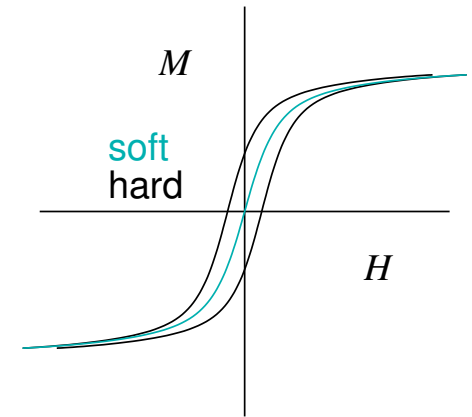
Superconducting phase diagram of $\text{Na}_x\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$

FePt nanoparticles for magnetic data storage — towards terabits per square inch

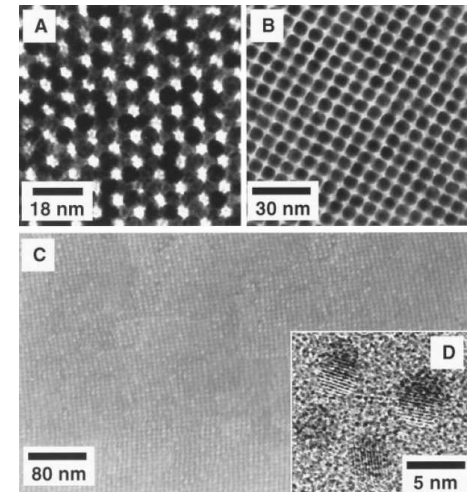
One of the challenges in developing new media for magnetic data storage is that when magnetic crystals/grains are made small (less than 10 nm usually) “hard” magnetic behavior is often lost and the coercive fields go to zero. Such behavior in small (nano) particles is often a characteristic of superparamagnetism.

Since data storage depends on magnetic memory, characterized by the coercive field, superparamagnets are useless.² However, high storage density ideally requires ordered arrays of well-separated magnetic nanoparticles. How does one make particles smaller without losing the coercive field? One way is to make use of materials with a high magnetocrystalline anisotropy K_u .

Sun *et al.* [S. Sun, C. B. Murray, D. Weller, L. Folks and A. Moser, Monodisperse FePt nanoparticles and ferromagnetic FePt nanocrystal superlattices, *Science* **287** (2000) 1989] have demonstrated the use of regular (self-assembled) arrays of monodisperse FePt nanoparticles as novel magnetic data storage media. FePt has a large K_u so small particles remain coercive. While pure Fe nanoparticles would rapidly oxidize in air, FePt nanoparticles are relatively air-stable. The authors have been able to use solution routes to prepare extremely monodisperse FePt nanoparticles. Both size and composition could be controlled in the synthesis. The authors also demonstrate that annealing arrays of the nanoparticles result in the small grain sizes being retained, while the coercivity increases.



M vs. H behavior for soft and hard ferromagnets



TEM and SEM images of the FePt nanoparticles.

²When the magnetic field is tuned off, the magnetic polarization of a soft ferromagnet or superparamagnet (not the same thing) will rapidly decay to zero.