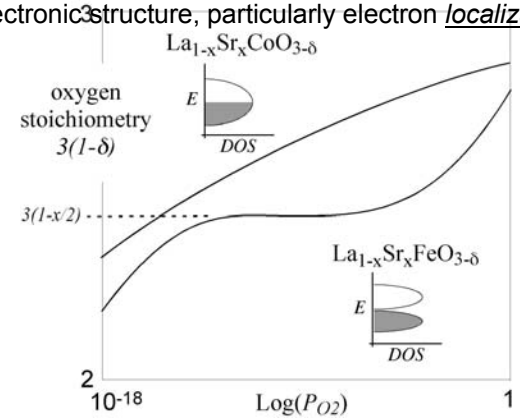
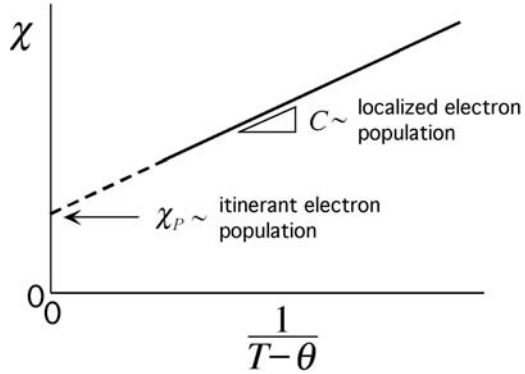
Electrochemical Ceramics - Understanding the Gap between Localized and Collective Viewpoints of Electronic Structure
CER/DMR/MPS - 0222002

S. B. Adler (PI), Department of Chemical Engineering, University of Washington

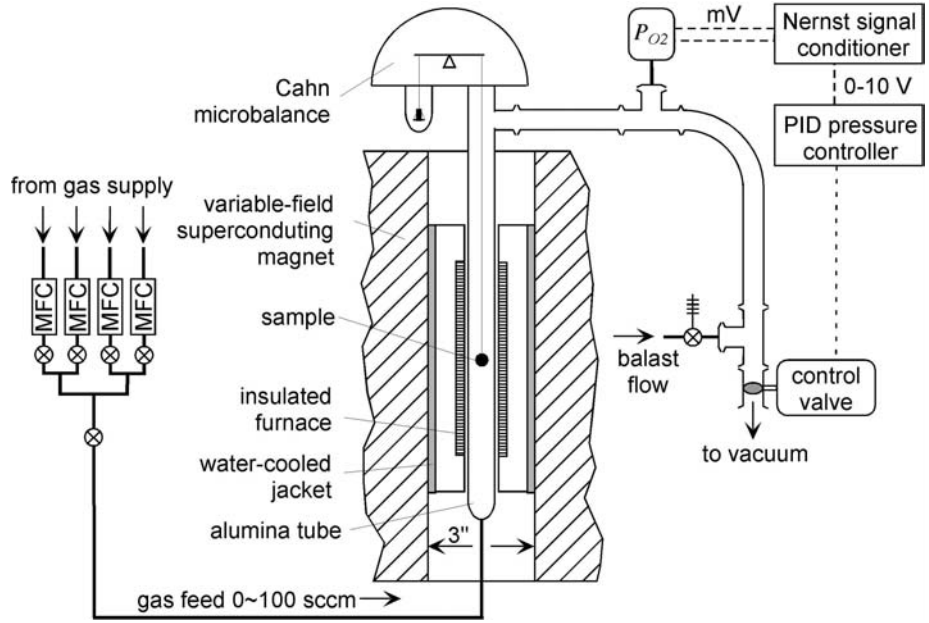
Many properties of Electrochemical Ceramics depend on electronic structure, particularly electron *localization*.



One way to distinguish localized and delocalized electronic states is by measuring *magnetic susceptibility*.



In order to measure magnetization in electrochemical ceramics, we are currently building a high-temperature, controlled-atmosphere Faraday balance magnetometer.



This system (the only one of it's type in the world) will allow very precise measurements of magnetic susceptibility over the range of temperature and P_{O2} of interest. Our goal is to measure and identify the relatively small contribution of band magnetism to the sample magnetization, and thus learn more about which electronic states contribute most to particular properties of electrochemical ceramics. This work will also contribute to our general understanding of electronic structure in highly defective materials, where neither band theory or point defect theory are fully obeyed.

Many properties of Electrochemical Ceramics depend on electronic structure, particularly electron localization. For example, this figure illustrates the dependence of oxygen vacancy concentration (δ), as a function of oxygen partial pressure (P_{O2}), for two transition metal perovskites $ABO_{3-\delta}$ (B = Fe or Co). In the case of cobalt, the 3d states of Co overlap to form a half-filled band (metal), with highly mobile delocalized electrons. In addition to being a very good electronic conductor, the oxygen vacancy concentration in this material depends continuously on P_{O2}, in a manner predictable using band theory. In contrast, for the case of B = iron, the 3d-states of Fe split due to electron repulsion (Hubbard U ~ 2.3 eV), causing a split in the band at Fe(III). Here there is a plateau in oxygen vacancy concentration, where free (but localized) holes and electrons are depleted. This also results in semiconducting behavior, with a minimum in the electronic conductivity. Many materials of technological interest (fuel cells, gas separation membranes) have a mixture of transition metals on the B site (e.g. both Co and Fe), where it can be very challenging to characterize the electronic structure as either localized or delocalized.

One way to distinguish localized and delocalized electronic states is by measuring magnetization. This figure shows a Curie-Weiss plot of magnetic susceptibility (χ) for a material containing a rigid (temperature independent) band structure. Localized electronic states polarize in the magnetic field, producing a $1/(T-\Theta)$ dependence, where Θ is a magnetic ordering temperature. In contrast, delocalized electronic states tend to exhibit a temperature-independent band magnetism, which results in a nonzero intercept as T is extrapolated to infinity. Thus by measuring magnetization as a function of temperature, P_{O2}, and dopant concentration, we may be able to "count" the number of localized and delocalized electronic states in the material.

In order to measure magnetization in electrochemical ceramics, we are currently building a high-temperature, controlled-atmosphere Faraday balance magnetometer. Unlike a SQUID (which is limited to low temperature), or a VSM (which has limited precision), a Faraday balance can achieve ppm resolution of the magnetization using a simple microbalance, given a sufficiently large sample, and a high magnetic field and magnetic field gradient. Features of our system (the only one of its type in the world) will include measurement temperatures to 1250°C, atmosphere and pressure control down to 10^{-3} Torr, sample mass up to 1 gram, magnetic field to 8 Tesla, and a field gradient of 1000 Gauss per inch. Our goal is to measure and identify the relative small contribution of band magnetism to the sample magnetization, and learn more about what electronic states contribute to the properties of electrochemical ceramics. This work will also contribute to our general understanding of electronic structure in highly defective materials, where neither band theory or point defect theory are fully obeyed.