Defect Clustering in Simple and Complex Oxides

Progress Report

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Title: Defect Clustering in Simple and Complex Oxides

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Progress Report

A. Technical Achievements

To facilitate in situ neutron diffraction studies of oxides, an environmental cell capable of 1673K under controlled atmospheres (1 atm total pressure) was constructed and successfully employed [1]. In addition, we continue to perfect our codes for correction and analysis of in situ single crystal diffuse x-ray scattering from oxides [2].

We have pioneered the development of a high oxygen pressure cell for simultaneous high oxygen pressure (1-35 atm) and high temperature transport studies. For example, using such a cell we successfully achieved $\delta=0.044$ in Co_{1-x}O at 32 atm oxygen and 1200°C [3]. With the advent of superconductivity in cuprates, which often require high oxygen pressure treatments, similar cells are now commercially available. We are currently modifying a Morris Research furnace for electrical property measurements to 200 atm.

On the theoretical front, we continue to develop our embedded cluster approach within the local density framework to model the energetics of defect structures in oxides [4]. We are now able to predict local lattice relaxation and geometries associated with defects. In addition, the details of electronic structure can be predicted and compared with experiment, e.g. X-ray near edge structure.

The strength and collaborative nature of our interdisciplinary program can best be illustrated by discussing our progress in simple and complex oxides (below).

Simple Oxides

In surveying m:n vacancy:interstitial clusters in Fe_{1-x}O such as the 1:1, 2:1, 4:1, 6:2, 7:2, and 13:4, our theoretical team showed the 7:2 cluster to be the most stable, followed closely by the 4:1 [5]. In situ powder diffraction patterns from Fe_{1-x}O were taken in a specially designed environmental cell at the Intense Pulsed Neutron Source (IPNS) at ANL [2]. Rietveld analysis of the numerous diffraction peaks permitted the interstitial population to be quite precisely established, and therefore the vacancy-to-interstitial ratio to be constrained. A distinction was therefore possible between proposed point defect clusters. The 4:1 prevails at high temperatures or at Fe-rich compositions, giving way to 7:2 and 10:3 clusters as the temperature or Fe content decreases. A small polaron conduction model, based upon the clusters detected, yielded excellent agreement with the measured electrical properties.

In Mn_{1-x}O , our theoretical effort predicted the 2:1 cluster to be the most stable among those surveyed, followed closely by the 6:2 (see above [5]). It should be stressed that this prediction was made prior to diffraction studies or electrical property modeling. In situ single crystal X-ray diffuse scattering from Mn_{1-x}O ($0 < x \leq 0.056$) at 1573K [1] showed no superstructure peaks or diffuse maxima in reciprocal space where such features occur in Fe_{1-x}O . For the first time, however, neutron powder diffraction patterns analyzed by Rietveld technique showed a definitive interstitial population of 2(1) percent at $x = .09$ in Mn_{1-x}O at 1323K [1]. The

vacancy-to-interstitial ratio of 5.5 is indicative of a mixture of small cation vacancy clusters and unassociated cation vacancies. Kröger-Vink modeling of the available nonstoichiometry data and our electrical property data (1673K) could be achieved with a combination of isolated cation vacancies, quadruply-charged $(6:2)^{''''}$ clusters, and a neutral $(m:n)^x$ species with $m-n=1$, e.g. $(1:0)$, $(2:1)$, etc. The ultimate interstitial content at $x=.09$ from this modeling is in good agreement with the Rietveld result. All three efforts--theoretical, structural, electrical--point to the existence of small vacancy:interstitial clusters in $Mn_{1-x}O$.

Despite considerable progress, the situation in $Co_{1-x}O$ remains unresolved at this time. Based upon an entire suite of physical property measurements--nonstoichiometry, cation tracer diffusion, electrical property measurements--in a high oxygen pressure cell [3] over the previously uninvestigated range of $0.003 \leq x \leq 0.044$, a new defect model was proposed [6]. Kröger-Vink modeling with isolated defects (V_{Co}^x , V_{Co}' , V_{Co}'') with or without Debye-Hückel interactions could not fit the data. Neither could a model without Debye-Hückel interactions but invoking clusters in addition to isolated vacancies provide a good fit. However, a model incorporating triply-charged $(4:1)^{''''}$ clusters with Debye-Hückel interactions fits all the experimental data quite well. At present there is no corroborating evidence for clusters in $Co_{1-x}O$. Theoretical calculations suggest the $(2:1)$ cluster to be the most stable associate in $Co_{1-x}O$ [5]; diffraction studies at these high pressures have yet to be attempted (see below).

Complex Oxides

We have made considerable progress on the $n=1$ phases of the $RE_2AE_{n-1}Cu_nO_{2n+2}$ series (RE =rare earth, AE =alkaline earth). Our in situ electrical measurements of $La_{2-x}Ba_xCuO_{4\pm\delta}$ were reported some time ago [7]. A schematic point defect model and Brouwer diagram were subsequently outlined in [8]. The model involves O_i'' at low dopant concentrations, the expected $p=[Ba_{La}']$ regime at intermediate concentrations, and V_O'' or associates, e.g. $(V_O''Ba_{La}')'$ at high concentrations. A similar model has also been proposed by Maier and Tuller [9]. We are currently testing this model against nonstoichiometry data (see proposed research); diffraction experiments will be conducted in the future (see below).

We also recently reported high temperature electrical property data for the $Nd_{2-x}Ce_xCuO_{4\pm\delta}$ solid solution [10]. The defect behavior appears to be a mirror image of that in $La_{2-x}Ba_xCuO_{4\pm\delta}$. Oxygen vacancies predominate at low doping levels, giving way to the $n=[Ce_{Nd}]$ regime at intermediate levels, and oxygen interstitials (or possibly associates) at high doping levels. A schematic point defect model and Brouwer diagram have been proposed [8].

There are important practical ramifications of the point defect structure in $Nd_{2-x}Ce_xCuO_{4\pm\delta}$ for high T_c superconductivity. Jorgensen and coworkers have suggested the co-existence of two sub-phases in this solid solution, based upon Rietveld analysis of neutron diffraction patterns [11]. To probe local atomic arrangements in this system, diffuse X-ray scattering experiments have been initiated at the National Synchrotron Light Source (NSLS) located at Brookhaven National Lab (BNL). Some 3000 data points were sampled in a volume of reciprocal space at two energies near the Cu-K absorption edge. By taking the difference, all pairs except those involving Cu were eliminated. The first aim of this work was to determine distortions in the CuO_2 plane. This a "tour de force" experiment, in that no one has yet attempted a quantitative analysis of diffuse scattering from a tetragonal ceramic crystal with so large a number of atoms in the unit cell. It is too early to say more than that there are unusual features in the diffuse intensity maps. Assuming this analysis proves fruitful, the Nd and Ce edges will be probed for local order about these sites.

In parallel with the electrical and structural efforts, the electronic structure of La_2CuO_4 -based (and other) cuprates has been explored via the embedded cluster/local density approach [12-14]. The effective valence of Cu was investigated, in conjunction with high quality X-ray absorption near edge studies. A simple linear relation between calculated Cu net charge and X-ray "characteristic energy" was found, which permits easy identification of Cu valence state. The absence of Cu^{3+} signal either in theory or in experiment helps to narrow the range of plausible superconductivity mechanisms.

In support of the collaborative effort with D. J. Lam and coworkers at ANL, the electronic properties of pure and transition metal-doped $\alpha\text{-Al}_2\text{O}_3$ (sapphire) were calculated. The convergence rate of one-electron and energetic (total energy) properties vs. cluster size and geometry was investigated in bulk material [15]. Building upon this work, the electronic structure and energetics of the experimentally important (0001) and (0112) surfaces were studied [16]. Using the idea of neutral "surface building blocks," a way was found to rationalize and predict the relative stability of possible cleavage planes. These results are proving useful for understanding which low energy surfaces can be formed to stimulate epitaxial growth of oxides on sapphire substrates. Attempts to predict the local minimum energy geometry and the related lattice relaxation mechanisms are underway.

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Appendix A

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Appendix A

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