Understanding atomic disorder in polar and magnetic oxides

My research provides structural descriptions of materials that cannot be described by traditional crystallographic tools due to disorder on the nanoscale. Deviation from a "well-behaved" crystalline lattice can be an intrinsic property of a material or a hallmark of a transition. I use large-box local structure modeling of the pair distribution function (PDF) to examine how materials behave from an atom's-eye point of view. Here I describe two chapters of my thesis: local dipoles in the frustrated "charge ice" $Bi_2Ti_2O_7$ and the metal-insulator transition in VO_2.

Pair distribution function analysis of crystalline materials has begun to flourish in the past decade after construction of the NPDF and GEM instruments at Los Alamos and ISIS, respectively. The advantage of the PDF method is its ability to probe structural details that lack long range-correlations.

Most oxide PDF analysis is performed with small-box, least-squares fitting. However, describing complex disorder using small unit cells can be cumbersome, if not impossible. I avoid this problem by analyzing PDF data via large-box reverse Monte Carlo (RMC) simulations. Atomic positions rearrange stochastically to best fit the experimental data, which includes both the Bragg profile and the PDF. The software and procedures had been established for data collected at ISIS, but I was the first external user to adapt them for the use of spallation data from Los Alamos and X-ray scattering data from the Advanced Photon Source. Since then, I have given my data conversion tools to fellow users and their own RMC projects are under way.

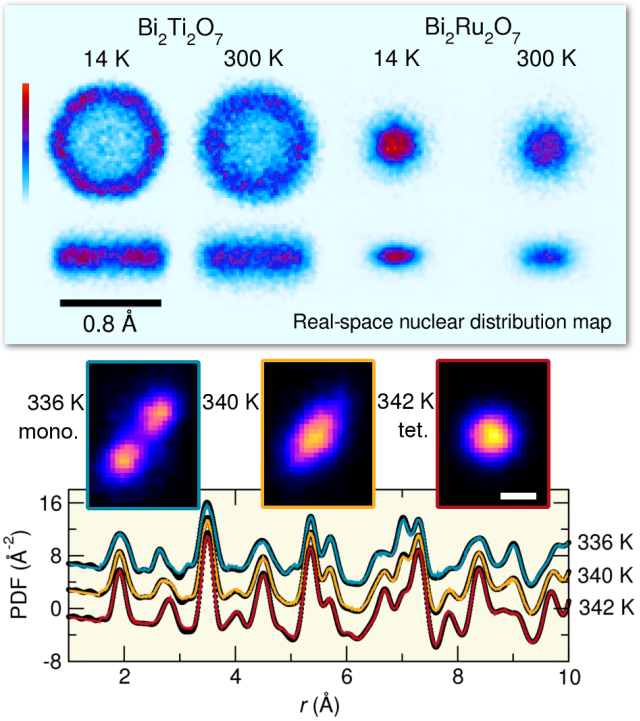

Figure 1: **Top**: Bi distributions are shown parallel and normal to O–Bi bonds. $Bi_2Ti_2O_7$ has large 0.4 Å off-centering (local dipoles), but $Bi_2Ru_2O_7$ is more compact. **Bottom**: X-ray RMC maps of V dimerization across the metal-insulator transition reveal it to be first-order (monoclinic to tetragonal), with no intermediate phase.

Figure 1 shows how local structural modeling of the PDF provides insight into $Bi_2Ti_2O_7$, a structurally frustrated system where electronic dipoles on Bi^{3+} exist solely on the nanoscale. This is an electronic analog to the uncompensated "magnetic monopoles" in $Dy_2Ti_2O_7$. Below, the real-space maps of V positions in VO_2 reveal that only the two end-member phases are present during the metal-insulator transition, with no intermediate.

I synthesize samples, collect data, perform simulations, and analyze the supercells myself. I presented four invited talks in 2010, including one at the BCA meeting in Warwick, and received a Graduate Student Gold Award at the Materials Research Society Fall Meeting.

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2. D. P. Shoemaker, R. Seshadri, A. L. Hector, A. Llobet, Th. Proffen, and C. J. Fennie. Atomic displacements in the charge ice pyrochlore $Bi_2Ti_2O_6O'$ studied by neutron total scattering. *Phys. Rev. B*, 81(14):144113(1–9), 2010.
3. D. P. Shoemaker, E. E. Rodriguez, R. Seshadri, I. Sabaj Abumohor, and Th. Proffen. Intrinsic exchange bias in $Zn_xMn_{3-x}O_4$ ($x \leq 1$) solid solutions. *Phys. Rev. B*, 80(14):144422–9, 2009.
4. D. P. Shoemaker, J. Li, and R. Seshadri. Unraveling atomic positions in an oxide spinel with two Jahn-Teller ions: Local structure investigation of $CuMn_2O_4$. *J. Am. Chem. Soc.*, 131(32):11450–11457, 2009.