Lugg,[a] Andrew V. Martin,[b] Scott D. Findlay,[c] J. M. LeBeau,[d] Susanne Stemmer,[e] [a]*School of Physics, University of Melbourne, Victoria (Australia).* [b]*Center for Free-Electron Laser Science, DESY, Hamburg (Germany).* [c]*School of Engineering, The University of Tokyo, Tokyo (Japan).* [d]*Materials Science & Engineering, North Carolina State University, Raleigh, NC (U.S.A.).* [e]*Materials Department, University of California, Santa Barbara, CA (U.S.A.).* E-mail: lja@unimelb.edu.au

Thermal scattering (due to phonon excitation) plays an important role in transmission electron microscopy and convergent-beam electron diffraction patterns. It makes the dominant contribution to Z-contrast (high-angle annular dark field) measurements in scanning transmission electron microscopy. Recent experimental advances have put Z-contrast imaging on an absolute scale [1] and structures can be solved and the atoms in a column counted to an accuracy of ±1 atom [2]. The results in Ref. [2] relied on simulations of thermal scattering using the frozen phonon model. Within this semi-classical model "the electron sees a snapshot of the atom frozen midvibration" [3]. Each electron "sees" a different configuration, and the contributions of different electrons are summed incoherently in the detector plane. Furthermore the frozen phonon model does not contain within its conceptual framework the momentum or energy transfer one would normally associate with inelastic scattering (in this case phonon excitation).

The correct model for thermal scattering is based on many-body quantum mechanics, as expressed by the equations of Yoshioka [3], with phonon excitation treated as a quantum excitation of the crystal during which the incident electron is inelastically scattered. We use an approximation similar to the Born-Oppenheimer-type approximation used in molecular physics for the many body wave function to derive a model for electron diffraction and imaging which can explicitly calculate the elastic component and the many inelastic components of the scattered electron wave. Our model predicts the scattered probability distributions for a single electron, including multiple elastic and inelastic phonon scattering to all orders. This is an advantage over other approaches based on the Yoshioka formalism in which, to allow for tractable calculations, the single inelastic scattering approximation is made.

Our model leads to a scattering intensity which is numerically similar to that calculated using the frozen phonon model and we provide a perspective on why this is the case, albeit that the two models have quite different conceptual underpinnings. Therefore our model underpins the integrity of the recent progress in the use of quantitative Z-contrast imaging to solve structures.

We will present several examples of how (crystalline) structures can be solved using quantitative Z-contrast imaging.

[1] J.M. LeBeau, S.D. Findlay L.J. Allen, S. Stemmer, *Phys. Rev. Lett.* **2008**, *100*, 206101 [2] J.M. LeBeau, S.D. Findlay, L.J. Allen, S. Stemmer, *Nano Letters* **2010**, *10*, 4405-4408 [3] R.F. Loane, P. Xu, J. Silcox, *Acta Crystallographica A*, **1991**, *47*, 267-278 [4] H. Yoshioka, *Journal of the Physical Society of Japan,* **1957**, *12*, 618-628 [5] B.D. Forbes, A.V. Martin, S.D. Findlay, A.J. D'Alfonso, L.J. Allen, *Physical Review B*, **2010**, *82*, 104103.

Keywords: modelling, thermal, scattering

MS.69.2

Acta Cryst. (2011) A**67,** C156

$SrTiO_3$ surface structures from diffraction & DFT: Homologous Series & Glasses

Laurence D Marks, *Departament of Materials Science and Engineering, Northwestern University, Evanston, IL, (USA).* E-mail: L-marks@northwestern.edu

Understanding the structure of oxide structures has proved difficult. Part of this is the technical direct methods of how to handle datasets with relatively large numbers of missing reflections (up to 50%), where the missing reflections may be strongest ones but overlap with bulk reflections which are orders of magnitude larger. A second issue is how to solve a structure when the exact number of atoms involved is not known. Lastly, there is the question of how to validate a structure, which in most cases has involved using Density Functional calculations where there can be very severe errors in the energies due to inaccuracies in the exchange-correllation potentials which is a particularly hard problem for oxides.

A very recent advance has been the realization that oxide surfaces are not that different from inorganic bulk oxides. In particular, it has turned out that the classic method of Bond Valence Sums in fact works remarkably well, and can have predictive power in clarifying what are reasonable or unreasonable direct methods solutions [1], [2]. This can be combined with better methods of calculating the energetics of oxide surfaces using more advanced methods with hybrid exact-exchange functionals (e.g. [3] and references therein) which are rather important as this more correctly represents the ionicity of the system; simpler functionals make oxides much too covalent.

Combining these, we have started to make some inroads into oxide surface structures. One specific case is the determination of a full homologous series of nx1 reconstructions on the $SrTiO_3$ (110) surface [1], in essence a monolayer equivalent of homologous series in bulk oxides. A second is the determination of a complicated ($\sqrt{13}\times\sqrt{13}$) R33.7º reconstruction on the $SrTiO_3$ (001) surface [4] which is a prototype structure of a series of glass-like tilings, again very similar to bulk glasses at the monolayer level. In all cases the bond valence sums at the surface are good, and the DFT energetics indicate that these are low-energy stable structures.

[1] J.A. Enterkin, A.K. Subramanian, B.C. Russell, M.R. Castell, K.R. Poeppelmeier, L.D. Marks. *Nature Materials,* **2010,** *9,* 245-248. [2] J. Enterkin, K.R. Poeppelmeier, L.D. Marks, **2011**. [3] L.D. Marks, A.N. Chiaramonti, F. Tran, P. Blaha, *Surf. Sci.* **2009,** *603,* 2179-2187. [4] D.M. Kienzle, A.E. Becerra-Toledo, L.D. Marks. *Physical Review Letters,* in press, **2011**.

Keywords: Surfaces, DFT, TED

MS.69.3

Acta Cryst. (2011) A**67,** C156-C157

JANA2006 as a unique tool to refine nuclear and/or magnetic structures using ToF data

Olivier Gourdon,[a] Ashfia Huq,[b] Jason Hodges,[b] Luke Heroux,[b] [a]*Juelich Center for Neutron Science outstationed at SNS, Oak Ridge (USA).* [b]*Oak Ridge National Laboratory, Oak Ridge (USA).* E-mail: gourdonoa@ornl.gov

Powgen represents a departure from previous designs for a time-of-flight powder diffractometer at a spallation neutron source and may be considered as a third-generation design. The geometric design of the instrument allows for all detected scattered neutrons to be focused onto a single diffraction profile yielding high count rate while preserving good resolution $\Delta d/d$ = 0.0015 at a d = 1 Å. The settings differ in the center wavelength, λ_{CW}, of neutron band chosen, each band being of ~ 1 Å width with Powgen chopper system operating at 60Hz. Full diffraction profiles need to be fitted using a peak shape based on convolution of back-to-back exponentials with a pseudo-Voigt. The use of a cold cryogenic moderator (and to lesser extent supermirror guide) yields significant differences in the d-space dependencies of the exponential rise (α) and decay (β) terms as well as the correction needed for reflection position, compared to the standard dependency functions modeled in GSAS [2]. Therefore, alternate functions for α, β, and