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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.

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SrTiO₃ surface structures from diffraction & DFT: Homologous Series & Glasses

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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-correlation 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 $n \times 1$ reconstructions on the SrTiO₃ (110) surface [1], in essence a monolayer equivalent of homologous series in bulk oxides. A second is the determination of a complicated ($\sqrt{13} \times \sqrt{13}$) R33.7° reconstruction on the SrTiO₃ (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.

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

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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

ΔT dependencies [3] need to be fitted by least squares minimization. JANA2006 has recently with success implemented this new approach to rigorously refine these parameters for calibration purpose. This presentation will compare the approach between JANA2006, Fullprof [4] and also GSAS.

In the second part of the presentation we will discuss the advantage of the new approach using magnetic superspace groups introduced into the JANA2006 software. Such tool is adequate with high resolution data which highlights more complex magnetic ordering.

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Fitting a square peg into a round hole: Simulating a modulated protein crystal

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We are interested in solving a protein crystal structure that contains an incommensurate modulation in one direction, a so-called (3+1) dimensional modulation. Several roadblocks in this structure determination have been found and will be solved by simulating this type of crystal and diffraction data. In the world of small molecules, modulated datasets are handled in a routine fashion. The existing software supplied with most X-ray systems can index the satellite reflections with the associated q-vectors, predict, integrate and scale the data. Then the Jana software suite can refine and solve the modulated small molecule structure. The resulting data can be neatly stored into a CIF file and submitted for archival and publication.

For protein crystallography it is an entirely different situation. Great strides have been made in processing modulated macromolecular diffraction data. Most protein data processing software cannot handle satellite reflections but the recently released EVAL15 software can process incommensurately modulated data for both protein and small molecules. Then SADABS can be purchased as standalone software to scale the resulting indexed and integrated values from EVAL15 producing an HK6 file. The HK6 format contains up to 6 indices (HKL + 3 q-vectors). It is at this point that there is currently no pathway for solving an incommensurately modulated protein crystal. Incommensurate protein models cannot be fit to 4D electron density maps, these structures cannot be refined against the modulated diffraction data and even if they could it would not be possible to store the structure in existing mmCIF or PDB formats. Thus significant modifications of existing tools are required to enable the solution of the first incommensurately modulated protein structure.

As a first step we are in the process of creating a (3+1)D training set that can be used to test approaches for modeling and refining a modulated protein structure against the corresponding diffraction data. The procedure to create the training dataset is backwards from normal data processing. First a modulated structure is generated and then the

resulting main and satellite reflections are simulated. The reflections are represented in (3+1)D indexing. Then everything needs is written into a CIF-type format that can be read in and used by protein crystallographic software. The problems we have encountered as well as the solutions we have selected will be presented and evaluated. The overall result was that each step of the process was much more challenging than we had initially envisioned.

Keywords: modulation, CIF, simulation, incommensurate

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Higher-dimensional crystallography of n-fold quasiperiodic tilings (n=7-15)

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The study of periodic average structures gives periodic lattices which closely correspond to the quasiperiodic tilings. This concept is of particular interest for the study of geometrical aspects of quasicrystal-to-crystal phase transformations [1], formation and understanding of quasicrystal-crystal interfaces [2], as well as the intrinsic band-gap behavior of phononic or photonic quasicrystals [3], [4]. For a general overview, see e.g. [5]. A detailed discussion on the periodic average structures of the Penrose and Ammann tiling (pentagonal, resp. icosahedral symmetry), as well as the Fibonacci sequence, can be found in [6].

We studied two-dimensional quasiperiodic tilings with heptagonal, octagonal, enneagonal, decagonal, hendecagonal, dodecagonal, triskaidecagonal and pentakaidecagonal symmetry with regard to their periodic average structures. By identifying the best (most representative) periodic average structures for each case, we have found that quasiperiodic tilings with different symmetries can show significantly different degrees of average periodicity.

The complexity of the periodic average structures and the degree of average periodicity depend on the minimum dimensionality and topological constitution of the hypersurfaces. The distribution of deviations from periodicity is given by the projected volume function of the higher-dimensional hypersurfaces upon physical space. The octagonal, decagonal and dodecagonal tilings show the smallest deviation from their periodic average structures. They have two-dimensional hypersurfaces, and the distribution of deviations can be described by simple sep-functions.

In the 7-, 9-, 11-, 13- and 15-fold tilings, the dimensionality of the hypersurfaces is greater than two, and is therefore reduced in the projection upon a two-dimensional space. This results in a non-homogeneous distribution of deviations from the periodic average lattice, and therefore in a higher complexity of the periodic average structures. But while the 7- and 9-fold tilings can still be described reasonably by at least one periodic average structure, the 11-, 13-, and 15-fold cases show a very low degree of average periodicity. A representation of the infinite tilings by their periodic average structures is generally unfavorable for systems of such high dimensionality. The concept of a periodic average structure can here best be used on finite systems like in photonic and phononic quasiperiodic crystals. The infinite systems on the other hand, show deviations from the periodic lattice that densely fill the unit cell of the later. However, the distribution of deviations is highly inhomogeneous. The study of periodic average structures gives therefore still information about which periodic lattices match the quasiperiodic ones best.

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