ABSTRACT

Crystallographic perturbations to valence charge density and hydrogen-surface interactions

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The subject of surfaces has been the epicenter of numerous studies in recent years, particularly with respect to applications in catalysis, thin films, and self-assembly of nanostructures where the surface-to-volume ratio is large. Understanding how the atomic structure of materials differs at surfaces where the atoms are far less constrained can yield fundamental insight into these interesting nanoscale phenomena. Quantum surface crystallography takes this one step further in an attempt to experimentally measure the structure of the electrons themselves, which is of greater importance than atomic positions in determining material properties.

We report a procedure for obtaining a much better initial parameterization of the charge density than what is possible from a neutral atom model. This procedure involves the parameterization of a bulk charge density model in terms of simple variables such as bond lengths, which can then be transferred to the problem of interest, for instance a surface.

Parameterization is accomplished through the fitting of Density Functional Theory calculations of a variety of crystal distortions to a bond-centered pseudoatom (BCPA) model. This parameterized model can then be applied to surfaces or for other problems where an initial higher-order model is needed without the addition of any extra fitted parameters.

Through the use of the BCPA model, we report a three-dimensional charge density refinement from x-ray diffraction intensities of the Si (001) 2x1H surface. By properly accounting for the covalent bonding effects in the silicon structure, we were able to stably refine the positions of hydrogen atoms at this surface in three dimensions, which had never before been accomplished for any surface. In addition, we found experimentally an increased, slightly localized bond density of approximately 0.31 electrons between each Si atom pair at the surface. Both the atomic positions and the charge density were found to be in remarkably good agreement with density functional theory (DFT) calculations.

The BCPA model was also applied to an experimental refinement of the local charge density at the Si (111) 7x7 surface utilizing a combination of x-ray and high energy electron diffraction. By perturbing about the bond-centered pseudoatom model, we found experimentally that the adatoms were in an anti-bonding state with the atoms directly below. We were also able to experimentally refine a charge transfer of 0.26 ± 0.04 e^- from each adatom site to the underlying layers. This was the first statistically significant refinement of site-specific bonding information at any surface utilizing x-ray diffraction data.

Precession electron diffraction (PED) is a technique which is gaining increasing interest due to its ease of use and reduction of the dynamical scattering problem in electron diffraction.

To further investigate the usefulness of this technique, we performed a systematic study of the effect of precession angle on the mineral andalusite where the semiangle was varied from 6.5 to 32 mrad in five discrete steps. We have shown that the intensities of kinematically forbidden reflections decayed exponentially as the precession semiangle (φ) was increased. Additionally, we have determined that charge density effects were best observed at moderately low angles (6.5-13 mrad) even though PED patterns became more kinematical in nature as the precession angle was increased further. We have also shown that the amount of interpretable information provided by direct methods phase inversion of the diffraction data increases monotonically but non-systematically as φ increases.

We report an experimental and theoretical analysis of the $\sqrt{3}x\sqrt{3}$-R30^o and 2x2 reconstructions on the MgO (111) surface combining transmission electron microscopy, x-ray photoelectron spectroscopy, and reasonably accurate density functional calculations using the meta-GGA functional TPSS. We have not only conclusively solved the atomic structures of these reconstructions, but have developed a kinetic model for an evolutionary pathway between structures driven entirely by exchange of water molecules between the surface and the environment that does not require the cations to move when the structure transforms. This is the first time an experimentally and theoretically supported kinetic model has described not only all of the structures in a series on a single oxide surface, but also describes why none of the structures pass through the thermodynamically most stable configuration.

Lastly, we have investigated the observability of valence bonding effects in aberration-corrected high resolution electron microscopy (HREM) images along the [010] projection of the

mineral Forsterite (Mg_2SiO_4). Direct observability of bonding effects would be both faster and less ambiguous than the refinement of similar features against diffraction data. Through analysis of simulated high resolution electron microscopy images, we have determined that bonding effects should be observable at levels approaching 20% of the total contrast. Initial experimental results for this material system have also been presented.

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