Towards a new quantitative probing tool: merits of combining DFT and quantitative electron diffraction

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Electron diffraction is very sensitive to the distribution of valence charge compared with x-rays at small scattering angles, as suggested by the Mott formula [1]:

\[ f_{el}(s) = \beta[Z - f_x(s)]/s^2 \]  

where \( f_{el}(s) \) and \( f_x(s) \) are the atomic scattering amplitudes for electron diffraction and x-ray diffraction, respectively, \( s = \sin\theta/\lambda \) is the scattering vector (\( \text{Å}^{-1} \)), \( Z \) is the charge of nucleus, and \( \beta \) is a coefficient, equal to 0.023934 if the units of \( f_{el}(s) \) and \( f_x(s) \) are \( \text{Å} \) and electron charge (e), respectively. The basic reason for the sensitivity in electron diffraction is the near cancellation of the scattering from the positively charged nucleus and the negatively charged electrons. Thus, small changes in electron density lead to large changes in scattering. The well-known divergence at small scattering angles for Coulomb scattering partly overcomes the near-cancellation, leading to strong measurable scattered intensities. Fig. 1 shows the critical scattering vectors for many elements (from H to Xe), below which electron diffraction is more sensitive to charge redistribution than is x-ray diffraction [2].

Electron diffraction and x-ray diffraction are complementary techniques. The latter undergoes a large extinction in low-order Bragg reflections (which are sensitive to chemical bonding), but can be used to accurately measure the structure factors of high order reflections (which are sensitive to atomic coordinates and temperature factors). Therefore, crystal structure and the Debye-Waller factor (related to thermal effects) can be determined by x-ray diffraction. As discussed above, quantitative electron diffraction enable to measure the low-order structure factors very accurately, thus providing valuable information on the distribution of valence electrons and chemical bonding. Moreover, due to the small probe size in TEM, this technique can access and measure charge distributions in nanocrystalline grains. Therefore, a combination of electron diffraction and x-ray diffraction will provide insight into the detailed charge distributions in functional materials [3,4].

Here, we show that, beyond charge density mapping, by taking advantage of the accurate measurement of electron structure factors, the combination of theoretical computations (e.g., DFT based on full-potential augmented plane-wave plus local orbitals method (Wien2k package)[5]) and quantitative electron diffraction can offer a unique quantitative approach for probing properties of materials. We give examples of how to apply this method to determine the charge ordering and orbital ordering in many functional materials, especially strongly correlated transition metal oxides, such as Na_{x}CoO_{2}, LaMnO_{3}, etc. Further, we demonstrate that accurately measured low-order electron structure factors can be used to test first-principles theories, especially to optimize exchange-correlation functionals, and the on-site Coulomb potential U in the LDA+U method.

References


Fig. 1 Critical scattering vectors (unit: angstrom$^{-1}$) for the elements H to Xe.