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Measuring Charge State at the Single-Atomic-Column-Base with Four-Dimensional Scanning Transmission Electron Microscopy

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Charge state influences many chemical and physical properties of an atom, such as the state of oxidation or reduction, the availability in forming bonds with other elements, or the ability to promote charge transfer. Engineering the charge state of atoms makes it possible to control the electronic, magnetic and chemical properties. For example, in catalysts, the surface charge state defines the chemical activity of an atom. For small gold clusters, the modification of electron orbits transforms the metallic bond into a covalent bond, converting gold into a non-metallic state.[1] Different approaches can be used to measure the charge states of atoms, including X-ray photoelectron spectroscopy, X-ray absorption spectroscopy, electron energy loss spectroscopy (EELS),[2] or scanning probe microscopy. The spectroscopic methods rely on the electron-orbital interactions, where the absorption of photon or electron energy reflects the status of orbital electron distribution. The X-ray based spectroscopic probes usually offer a spatial resolution of about micrometers, with location related properties mostly missing. While EELS in scanning transmission electron microscopy (STEM) can offer better spatial resolution, the detection sensitivity is limited by noise, making it even more challenging to measure the charge states of heavy elements such as Bi, Pb and Sr, where the major edges are around or more than 2000 eV. Recently, by coupling a high-speed pixelated electron detector with an aberration corrected STEM, electric field mapping can be obtained using scanning diffraction or four-dimensional (4D) STEM. Projection of charge density in two-dimension (2D) can be derived by using the divergence of the electric field map, here we show the possibility to detect the charge state of atoms using the charge density image.

Figure 1 illustrates the process of the charge state measurements, including the simulation of the scanning diffraction dataset (Fig. 1b) from a single Sr in $SrTiO_3$ with the thickness of one unit cell (Fig. 1a). The brighter annular region surrounding the Sr atom in Fig. 1b corresponds to the strong scattering of incident electrons by the nuclei. For each diffraction pattern, the shift of center of mass of the intensity is first determined, which is then converted to the change in electron momentum under the influence of the local field in the specimen. The electric field map surrounding the individual Sr atom is derived in Fig. 1c, inverse to the measured momentum transfer. The vectors show the direction and magnitude of local electric field. Note that the electric field is radially distributed as demonstrated by the colors and arrows, suggesting the high symmetry of local field around Sr. Based on the electric field map, we can construct the 2D projection of local charge density from Gauss's law in the 2D form,

$$\nabla \cdot E = (\partial E_x)/\partial_x + (\partial E_y)/\partial_y = \sigma/\varepsilon_0 \quad (1)$$

In experiments, the 4D STEM data was collected on a JEOL JEM 300CF (Grand ARM) double aberration corrected S/TEM operating at 300 kV; diffraction patterns were recorded with a Gatan OneView camera at the speed of 300 frames-per-second (fps), with 512x512 pixels for each frame. The semi-convergence angle was 26 mrad. Fig. 1d shows the 2D charge density map within a unit cell acquired from a $SrTiO_3$ sample. In the charge map, we measure the charge state atom by atom by

integrating the intensity surrounding the atomic column. Statistics of the measured charge intensity from model perovskite materials including $SrTiO_3$, and $PbTiO_3$, are shown in Fig. 2. The advantages of using 4D STEM to measure the charge state and how it is compared with results from EELS measurement and known values in their stoichiometric phase will be discussed.

In conclusion, with scanning diffraction data set acquired by high speed pixelated electron detector in aberration corrected STEM, 2D map of electric field and charge can now be achieved with high spatial resolution. By analyzing the local total charge surrounding an atom, we show the charge state can be measured at the level of single atomic column.

References:

[1] A. Wang, J. Li, T. Zhang, Nature Reviews Chemistry 2, 65 (2018)
[2] D. A. Muller, Nature Materials 8, 263 (2009)
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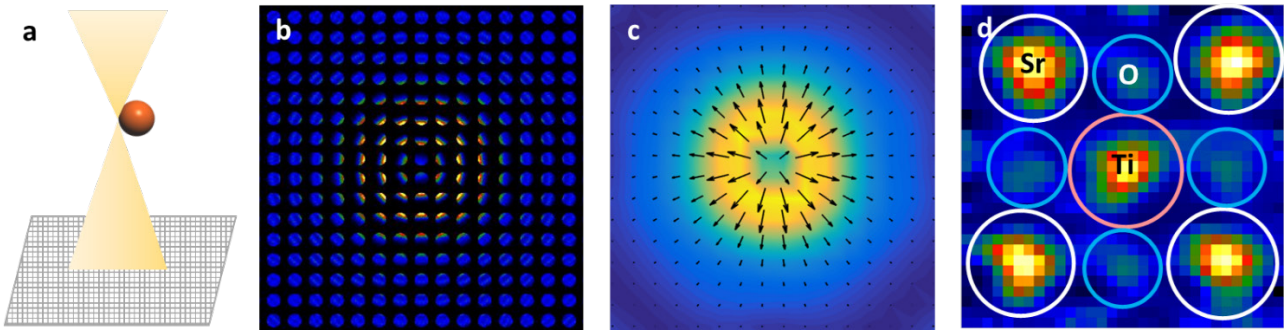

Figure 1. (a) The schematic showing the set-up of scanning diffraction in aberration corrected STEM. (b) Simulated scanning diffraction data set from a Sr atom in $SrTiO_3$. (c) The electric field map measured from (b). (d) Charge density image derived from the divergence of electric field map of a unit cell of $SrTiO_3$ in experiment, the highlighted areas are used to measure the total charge of Sr, O and Ti-O columns.

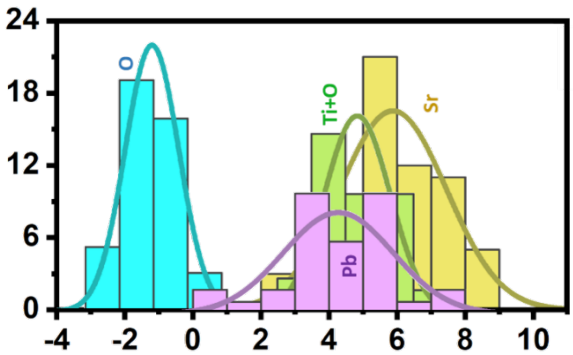

Figure 2. The histogram of total intensity measured for Sr, O, Ti-O, Pb atomic columns in the charge density images acquired with 4D STEM on $SrTiO_3$ and $PbTiO_3$.

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