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Mapping Valence Electron Distribution and Magnetic Field by 4D-STEM

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Measuring electron distribution is important for understanding the chemical bonding and the physical properties for quantum materials. Diffraction-based methods, including single crystal X-ray diffraction, combination of quantitative convergent-beam electron diffraction and X-ray diffraction, have been developed to measure the valence electron distribution of single crystals. These methods, however, require large single crystals which may not be available in many cases. The recently development of 4D-STEM in aberration corrected STEM has enabled the direct measurement of the charge density. The measurement is based on center-of-mass (COM) and only valid for extremely thin samples. Moreover, it only measures the projected total charge density rather than the valence electrons (VE) that bond the atoms together. Here, we demonstrate that the 4D-STEM is sensitive to the valence electron distribution, thus can be used to map aspherical VE distribution in a wide range of materials.

The electron density of a crystal can be modeled based on atom-centered multipole density functions (MDF) with the electron density of the atom as [1]:

$$\rho_{atom}(r,\theta,\varphi) = P_c\rho_{core}(r) + P_v\kappa^3\rho_{val}(\kappa r) + \sum_{l=0}^{l_{max}} \kappa'^3 R_l(\kappa' r) \sum_{m=0}^{l} P_{lm\pm} d_{lm\pm}(\theta,\varphi)$$

here ρ_{core} and ρ_{val} are the spherical atomic core and valence electron density, P_c and P_v are the electron population of core and valence component, κ is a parameter describing expansion or contraction of the valence shell. The third term is the multipole contribution, representing aspherical distribution of valence electrons with θ and φ being the angular coordinates of $\boldsymbol{r}$. Based on above formula, the corresponding structure factors can be calculated and used to simulate 4D-STEM patterns through either the Bloch wave method or the multislice method.

In 4D-STEM, the reflection disks heavily overlap, and form interference patterns that change with probe positions. For a typical convergent angle of 20-30 mrad, the central part of the disk, e.g., 0-30 mrad, has the best signal and carries VE information. Fig. 1 compares the VE distribution at (001) TiO_2 plane (Fig. 1a,b) as well as their corresponding 4D-STEM patterns calculated with the probe at O (Fig. 1c,e) and Sr (Fig. 1d,f) site between the MDF (top panel) and the IAM (bottom panel) models for $SrTiO_3$. Aspherical VE orbitals are clearly seen in the VE map (Fig. 1a) for the MDF model. The difference of the 4D-STEM patterns is significant between the MDF and IAM models, e.g., it shows a true 2mm symmetry in the pattern calculated using the MDF model (Fig. 1c), but a forged 4-fold symmetry using the IAM model (Fig. 1e) at O site. This indicates if done properly the 4D-STEM is sensitive to the VE distributions, and thus can be used to map VE distribution by refining 4D-STEM patterns using MDF [2].

The 4D-STEM technique has also been used to map the magnetic induction by measuring the shift of the bright field disks (BFD). Fig. 2a shows the magnetic induction map by COM method from 4D-STEM data for a square of permalloy ($Ni_{80}Fe_{20}$). The map is smeared by diffraction effect in the BFD in which the COM of the disk deviates from the geometry center of disk due to the diffraction effect, as shown in

Fig. 2b,c. Here, we will report a method that we developed to effectively remove the diffraction effect, as demonstrated in Fig. 2d.

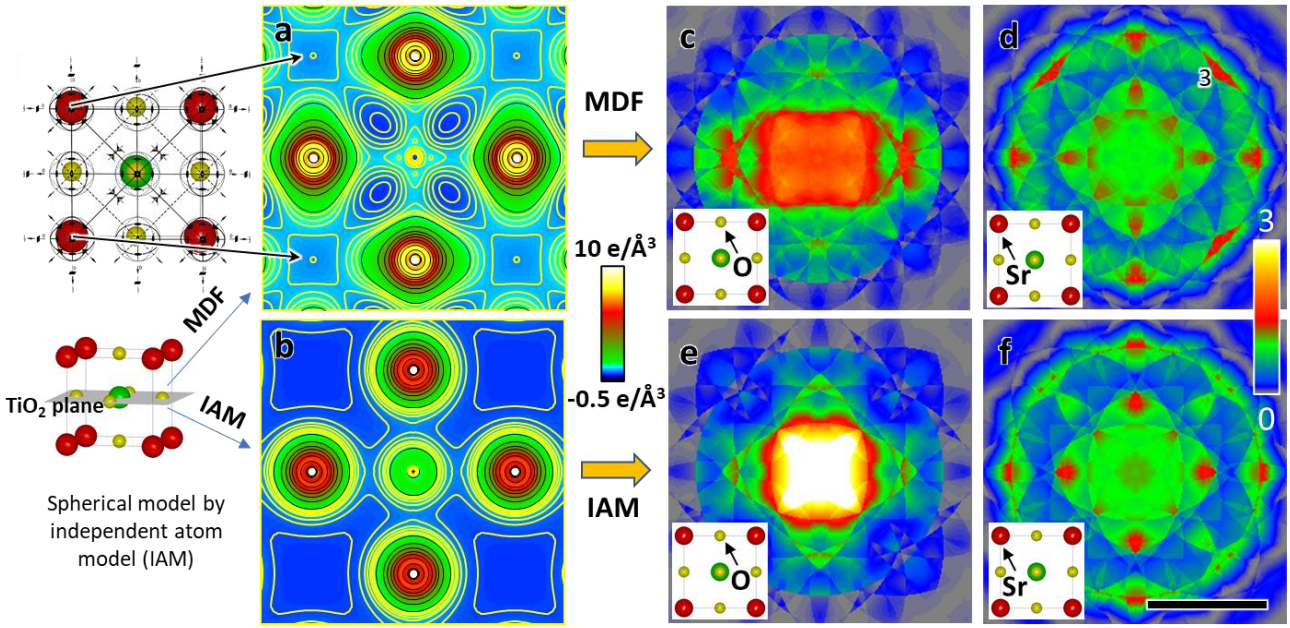

Figure 1. (a,b) Valence electron (VE) distribution of (001) TiO_2 plane of (a) aspherical VE model calculated based on multipole density functions (MDF) with Sr^{2+}, Ti^{3+} hexadecapole K_{41}=1 and $O^{1.67-}$ hexadecapole P_{44+}=1 and (b) spherical independent atom model (IAM). (c-f) [001] 4D-STEM patterns of $SrTiO_3$ with the probe at (c,e) O (0,½,½) site and (d,f) Sr site calculated based on (c,d) the MDF and (e,f) IAM model. The convergent angle is 21 mrad and the sample thickness is 10 nm. All patterns have the same scale with a scale bar of 21 mrad in (f). While the pattern at O site shows a forged 4-fold symmetry using IAM (e), it reveals a real 2mm symmetry using MDF (c).

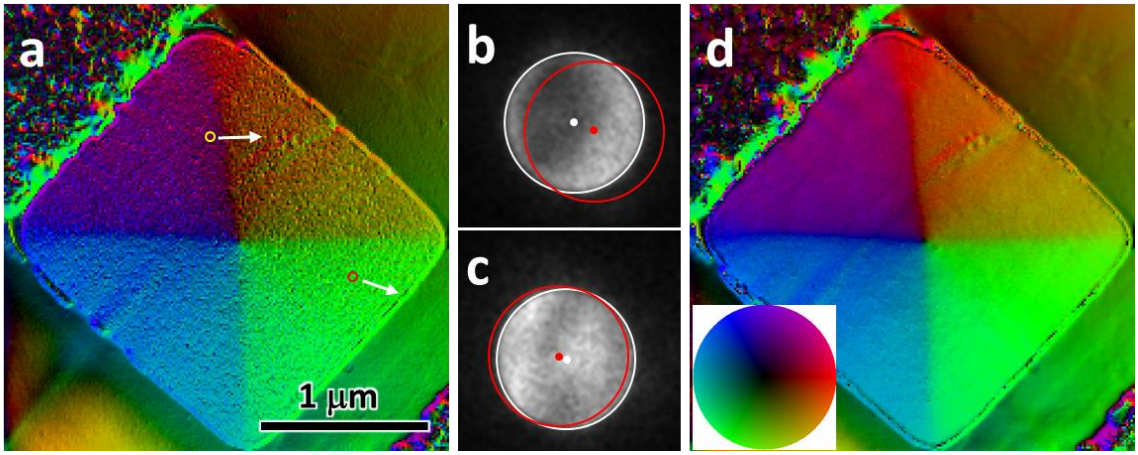

Figure 2. (a) A typical magnetic induction map from a 2µm square element of permalloy ($Ni_{80}Fe_{20}$) on the SiN obtained by the COM method. (b,c) 4D-STEM patterns from the position marked by (b) white and (c) red circles in (a). The geometry center (GC) and the COM of the disk are marked by white and red dots, respectively. Apparently, the COM deviates the GC due to the diffraction effect of the crystal grains. (d) Induction map with the method that effectively removes the diffraction effect. The maps are shown in color with the color wheel shown in (d). The top left corner is the Al grains of signal line for applying spin-current.

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