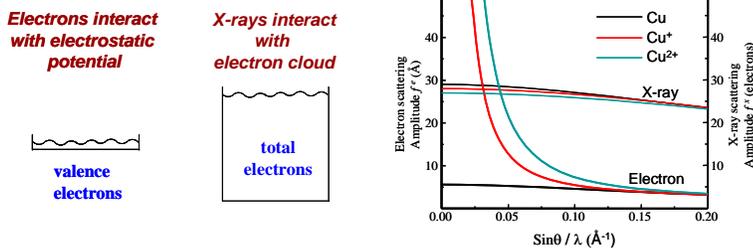


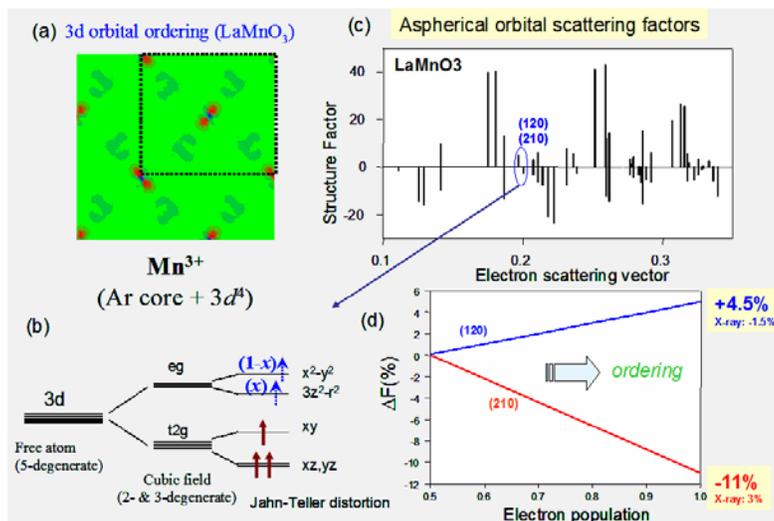
Sensitivity of electron scattering to valence charge distribution

The experimental charge density in materials can be measured using two complementary techniques; X-ray and electron-diffraction. X-ray diffraction (XRD) measures the total density of electrons in solids from the X-ray structure factors, which are the Fourier components of the electron density, while electron diffraction (ED) measures electron structure factors, the Fourier components of the electrostatic potential. Electron structure factors can be converted to x-ray structure factors using the Mott formula: $f^{(e)}(\mathbf{s}) = A[Z - f^{(x)}(\mathbf{s})]/s^2$. Structure factors at small scattering vector s , or scattering angle s ($s = \sin\theta/\lambda$), are difficult to measure accurately with x-ray diffraction in single-crystal experiments due to extinction, and also in powder diffraction (polycrystals with small grains). On the other hand, in a transmission electron microscope (TEM), a very small electron probe can be used to study a defect-free nanometer region in the sample, though quantitative analysis has been a challenge. The recent development of quantitative electron diffraction using convergent beam electron diffraction (CBED) and parallel recording of dark-field images (PARODI) has opened the door to mapping valence-electron distributions by accurately determining the structure factors of the innermost reflections. With CBED we record electron diffraction from a sample with a consistent thickness, which is relatively straightforward and suitable for small unit-cells. With PARODI, we analyze intensity oscillations of image-coupled diffraction patterns from a sample with varying thicknesses. The latter technique is more complex due to the thickness involved, nevertheless, it doesn't require a larger convergent-beam angle, and can be used for crystals with large unit-cell.

Here, we compare the sensitivities of electron- and X-ray scattering to charge distribution and orbital ordering. Our studies reveal the importance of accurate determination of low-order structure factors in valence electron-density study, and suggest the merit of the combined use of electron diffraction, X-Ray diffraction and DFT calculations for solids, especially those with large unit cells.



Comparison between electron and X-Ray scattering: electron diffraction is more sensitive to the charge transfer at small scattering angle than X-Ray diffraction



The sensitivity of electron structure factors to orbital ordering. (a) The real-space deformation charge-density maps (in the (001) plane) of LaMnO₃ obtained by DFT calculations show the e_g orbital ordering. (b) Orbital splitting with orbital ordering due to the different electron population in $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ of e_g orbital. (c) The electron structure factor (in units of Å) of LaMnO₃ as a function of the scattering vector (in units of Å^{-1}). (d) The relative changes of electron structure factors (210) and (120) as a function of electron population x in the $d_{x^2-y^2}$ orbital ($x=0.5$, no orbital ordering; $x=1.0$, full orbital ordering).

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