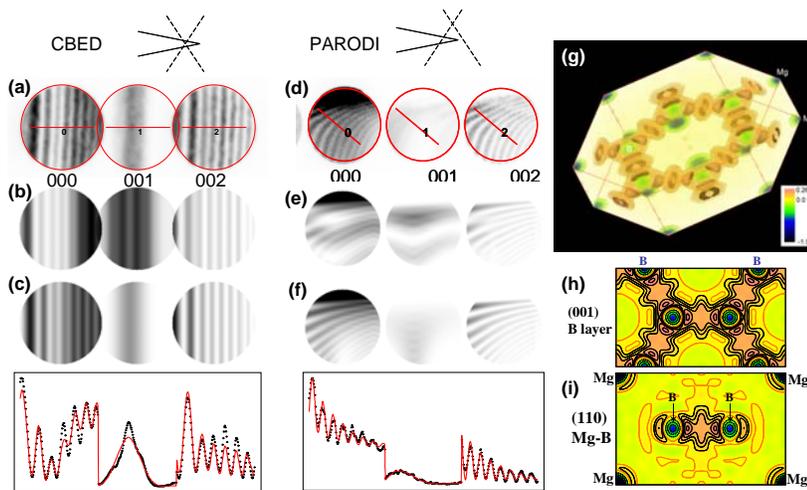


## Valence-electron distribution in MgB<sub>2</sub> by accurate diffraction measurements and first-principles calculations

A great challenge in the studies of condensed matter is to measure the redistribution of electrons that takes place when atoms assemble to form solids, and a good approximation is that only valence electrons are rearranged. Thus, if the x-ray structure factors are known, the valence electron distribution can, in principle, be determined directly by Fourier transform:  $\Delta\rho = \rho_m - \rho_a = \sum (\mathbf{F}_{gm} - \mathbf{F}_{ga}) \exp(2\pi i \mathbf{g} \cdot \mathbf{r})$ . Here, the subindex m refers to the ideally measured values of the structure factors  $F_g$  and of the electron density  $\rho(r)$  in the crystal, and  $a$  refers to the corresponding calculated values assuming unperturbed atoms. However, the extraction of sensible information about the valence-electron distribution requires, in addition to extremely accurate measurements of the amplitudes of the x-ray structure factors, also knowledge of their phases that are generally inaccessible from kinematical diffraction experiments. Electron diffraction of fast electrons offers a means of extracting the phases of the structure factors because of the strong dynamical coupling between different beams. Furthermore, in electron diffraction, those structure factors of reflections at small scattering angles are strongly influenced by the distribution of the valence electrons in the crystal. We use synchrotron x-ray and precision electron-diffraction techniques to determine accurately the structure factors of reflections that are sensitive to the valence-electron distribution in the superconductor MgB<sub>2</sub>. These values deviate significantly from those calculated using the scattering factors of free or neutral atoms, but agree well with our calculated structure factors based on density-functional theory (DFT). Having experimentally established the reliability of our first-principles-based structure factors, we present electron-density maps of the redistribution of the valence electrons that takes place when hypothetical free atoms of Mg and B in MgB<sub>2</sub> interact to form the real crystal.



Conventional convergent beam electron diffraction patterns (CBED): (a) experimental (b) calculated for procrystal, and (c) best fit to the experiment. Parallel recording of dark-field images (PARODI) patterns: (d) experimental, (e) calculated for procrystal, and (f) best fit to the experiment. Sketches of experimental setup for both methods using a wedge sample are included at the top of the figures. (g) A three-dimensional valence-electron distribution in MgB<sub>2</sub> based on precision electron-diffraction measurements and DFT calculations. (h-i) DFT calculated difference charge-density maps  $\Delta\rho$ .

L. Wu, Y. Zhu, T. Vogt, H. Su, and J. W. Davenport (Brookhaven National Laboratory)  
J. Taftø (University of Oslo, Norway)