s4.m14.o2   **Beyond Locating the Atoms Towards Addressing the Electronic Structure of Crystals Using Advanced Transmission Electron Microscopy.** J. Tafto[a], Lijun Wu, R. F. Klie and Yimei Zhu, *Center for Functional Materials, Brookhaven National Laboratory, PO Box 5000, Upton NY 11973-5000, USA, [a]Department of Physics University of Oslo, PO Box 1048, N- 0316 Oslo, Norway. E-mail: ljwu@bnl.gov*

Keywords: Electron Diffraction; Electron Density; EELS

With the present focus on nanostructures, the role of the transmission electron microscope (TEM) as a research tool is becoming increasingly important. Among the major strengths of TEM are the capability of obtaining diffraction patterns and electron energy loss spectra (EELS) from nanometer sized areas. In addition, advanced TEM may serve as a supplement to synchrotron x-ray diffraction and absorption spectroscopy in efforts to study bonding and electronic structure of bulk materials. This is in particular the case when only small-grained polycrystalline samples are available, but TEM may also provide valuable input in studies of single crystals. For example, the near edge fine structure at EELS absorption edges was used to locate different valence states of Fe within the unit cell of a mixed valence crystal already two decades ago [1], and more recently precision convergent beam electron diffraction (CBED) was used in combination with x-ray diffraction to study the spatial distribution of valence electrons in Cu_2O [2].

In this presentation, we report our recent study of the MgB_2 where we use both EELS [3] and CBED [4] to gain insight into the electronic structure of this new superconductor with T_c=39K. Using angle-resolved EELS we studied the fine structure at the K-edge of boron in order to probe the empty boron p_{xy} and p_z states near the Fermi level in this anisotropic hexagonal crystal. Similar information can be obtained using polarized soft x-rays in absorption spectroscopy (XANES) if sufficiently large single crystals become available. Using quantitative CBED we determine the structure factors at short g-vectors. These structure factors at short g-vectors, which are strongly influenced by the valence electron redistribution, can be determined with very high accuracy using electron diffraction. For example, after converting to x-ray structure factors, we measure F_{001} of MgB_2 to be 2.15±0.03 electrons while the calculated structure factor for the procrystal differs 20 standard deviations from this value (2.75 electrons). We also did DFT calculations, and found good agreement between experimental and theoretical structure factors.

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s4.m14.o3   **Quantitative Electron Diffraction in Studies of Electron Distribution in Crystals**. Yimei Zhu, L. Wu, J. Zheng, J. W. Davenport, and J. Tafto[1], *Center for Functional Materials, Brookhaven National Laboratory, Upton NY 11973-5000, USA, [1]Department of Physics, University of Oslo, PO Box 1048, N-0316 Oslo, Norway. E-mail: zhu@bnl.gov*

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Quantitative electron diffraction is a valuable supplement to synchrotron x-ray diffraction in studying the valence electron distribution in crystals. In particular, structure factors at short g-vectors that are strongly influenced by bonding and charge transfer, can be measured with high precision using electron diffraction. These accurate structure factors can be used in combination with synchrotron x-ray diffraction data and subsequent multipole refinement to determine valence electron distribution, or they may be used as the sole experimental data set to test and scrutinize the nowadays easily accessible first principle calculations of electronic structure and electron density. These quantitative electron diffraction measurements are based on convergent beam electron diffraction, either in the conventional way by focusing a small probe of fast electrons on a thin crystal area or by focusing the probe above the specimen to form shadow images within many diffraction discs simultaneously. We refer to these two quantitative methods as cCBED (conventional convergent beam electron diffraction) [1] and PARODI (parallel recording of dark-field images) [2]. The difference between these approaches is that the probe is focused on the specimen in cCBED, thus recording the pattern at a particular thickness, while it is focused above the specimen in PARODI, thereby illuminating a micrometer sized area to record the pattern over a range of thicknesses and suitable for both perfect crystals and defects. In recent years we have studied several materials using these techniques, many of them high Tc superconductors with large unit cells. For moderately short g-vectors the cCBED is straightforward since no thickness variation is involved. However, for crystals with very dense reciprocal rows PARODI is more preferable because the information content in cCBED is limited due to the very small convergent angle required to avoid overlap between the diffraction disks. The thickness variation in PARODI adds a new dimension in information where we observe the thickness fringes in many reflections simultaneously. We will present results from our study of the superconductors MgB_2 [3] and $YBa_2Cu_3O_7$, as well as $CaCu_3Ti_4O_{12}$ that exhibits highest static dielectric response ever observed.

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