

**PS09.01.31 CHARGE DENSITY STUDY OF NONLINEAR OPTICAL CRYSTALS: LBO, BBO AND KB5.** Hwo-Shuenn Shen<sup>1,2</sup>, Chih-Chieh Wang<sup>1</sup>, Chi-Rung Lee<sup>1</sup>, Yu Wang<sup>1,2\*</sup>, Alex Darovsky<sup>3</sup>, Robert Bolotovskiy<sup>3</sup>, Philip Coppens<sup>3</sup>, <sup>1</sup>Department of Chemistry, National Taiwan University, Taiwan, R.O.C., <sup>2</sup>Synchrotron Radiation Research Center, Hsinchu, Taiwan, R.O.C., <sup>3</sup>X3, National Synchrotron Light Source, BNL, Upton, New York, U.S.A.

Borate Compounds have attracted great attention recently because of its excellent UV-NLO (nonlinear Optical) properties. KB5(KB<sub>5</sub>O<sub>10</sub>H<sub>4</sub>·2H<sub>2</sub>O) is the first developed borate NLO crystal, while BBO (β-BaB<sub>2</sub>O<sub>4</sub>) and LBO (LiB<sub>3</sub>O<sub>5</sub>) are the best materials so far developed. All the three crystals are crystallized in noncentric space group of *Pna*21, *R3c*, and *Aba*2 for LBO, BBO, and KB5 respectively. Accurate single crystal diffraction data were measured at room temperature using MoKα and at ~50K using synchrotron radiation using 0.394Å for LBO; and at room temperature and 125K using MoKα for BBO and KB5 respectively. Charge density distribution studies were made in order to investigate the correlation between the electron density distribution and NLO property. The NLO properties of LBO, BBO and KB5 are believed to be mainly contributed from their anionic group, (B<sub>3</sub>O<sub>7</sub>)<sup>5-</sup>, (B<sub>3</sub>O<sub>6</sub>)<sup>3-</sup> and [B<sub>5</sub>O<sub>6</sub>(OH)<sub>4</sub>]<sup>1-</sup>. The distorted anionic groups are revealed from their bond distances and angles of BO<sub>3</sub> and BO<sub>4</sub>. Charge density distribution maps of the three title compounds are derived using the multipole model. The uneven charge density distribution of these anionic groups are clearly represented. A slight difference between the two 3-coordinated B of LBO is found. Highly polarized and delocalized of (B<sub>3</sub>O<sub>6</sub>)<sup>3-</sup> of BBO is clear detected. These uneven charge density distribution and polarization may correlate to their NLO property. The comparison on different wavelengths and different temperatures of the three compounds will be discussed.

**PS09.01.32 APPLICATIONS OF XD IN CHARGE DENSITY RESEARCH.** T. Koritsanzky, Institute for Crystallography, Free University of Berlin, Germany

An introduction to XD /1/, a Computer Program Package for Multipole Refinement and Analysis of Electron Densities from Diffraction Data, will be given. This new package is under development, within an IUCr project, and test versions have been available for the wide scientific community. The method of extracting electronic properties from Bragg reflections is based on precise X-ray diffraction data and non-conventional scattering formalism /2/. The procedure, due to the approximations involved, has limitations and the evaluation of the results, obtainable almost automatically, needs expertise. The lecture intends to help the "non-experts" to get familiar with the basic aspects of the method and the main features of the different programs. A general refinement strategy applicable almost routinely will be proposed with the emphasis also on testing the parameter estimates obtained. Examples will be given when constrained refinements increased the physical significance of the result. Several applications including full topological analysis of experimental electron densities and Laplacian functions will be presented.

/1/ T. Koritsanzky, S. Howard, P.R. Mallinson, Z. Su, T. Richter and N.K. Hansen: XD a Computer Program Package for Multipole Refinement and Analysis of Electron Densities from Diffraction Data, 1995.

/2/ N.K. Hansen and P. Coppens, Acta Cryst. A34, 909, 1978.

## Charge, Spin & Momentum Density II Comparison of Theory with Experiment

**MS09.02.01 BUILDING BRIDGES BETWEEN THEORY AND EXPERIMENT.** Mark A. Spackman, Department of Chemistry, University of New England, Armidale NSW 2351, AUSTRALIA

The comparison between theory and experiment has been a recurring theme of charge density analyses over the past three decades, and today we no longer expect that "if an experimental and a theoretical deformation map agree the most probable interpretation is that they are *both* wrong".<sup>1</sup> Nevertheless, we have reached the point where mere comparison no longer suffices. An important emerging issue in charge density analyses is to ascertain precisely what information can be obtained from the charge density experiment that could not have been derived, perhaps more reliably and economically, from theoretical calculations. Because of this it is timely to re-appraise the different roles of experiment and theory, to better understand their comparative advantages (and weaknesses!) and to explore ways in which both can contribute in a complementary fashion to yield more information together about a system than either could provide separately.

Various means of comparing theoretical and experimental charge density results will be reviewed in this lecture, with some examples taken from the recent literature, and some recent strategies using both together will be highlighted. It will be argued that we should perhaps be concentrating our efforts in directions where experiment and theory disagree the most, rather than focusing on their agreement (which, echoing the healthy scepticism above, is sometimes more apparent than real because of subtle uncertainties in either or both). In the realm of molecular crystals at least, this suggests that we begin to look seriously at the area of intermolecular interactions: their effect on the electron density and other properties, and obtaining meaningful estimates of their energies from the diffraction data. This would open a vast range of possible applications in highly active areas of modern chemistry such as supramolecular chemistry or zeolite catalysis, areas which are not yet accessible by accurate theoretical methods.

1. F.L. Hirshfeld, *J. Mol. Struct.* **130**, 125 (1985)

(the comment was attributed to W.N. Lipscomb, 1971)

**MS09.02.02 CORUNDUM BY DENSITY FUNCTIONAL THEORY AND HARTREE-FOCK CALCULATIONS.** Karlheinz Schwarz, Peter Blaha, Technische Universität Wien, A-1060 Vienna, Getreidemarkt 9/158, Austria, Roberto Dovesi, Department of Inorganic, Physics and Materials Chemistry, University of Torino, via Giuria 5, I-10125 Torino, Italy

Corundum, or α-Al<sub>2</sub>O<sub>3</sub>, is investigated by two *ab initio* methods, namely the linearized augmented plane wave (LAPW) method as embodied in the WIEN95 code, and the periodic Hartree-Fock (HF) LCAO scheme using the CRYSTAL program. In density functional theory (DFT) both, the standard local density approximation (LDA) and the more sophisticated generalized gradient approximation (GGA) are used. With these methods we study DFT vs HF, LDA vs GGA, different basis sets (analytic vs numerical) and numerical differences involved in WIEN95 and CRYSTAL.

We investigate the electronic structure and will show the band structure and density of states and discuss chemical bonding. We optimize the structure which agrees well with the experimental geometry for which the electron density and the corresponding static structure factors are obtained by all schemes mentioned above. The small variations in the electron density caused by these schemes can be visualized by difference electron densities. These state-of-the-art results provide a good basis for a comparison with experimental structure factors and density distributions.

The electric field gradient (EFG) is extremely sensitive to the anisotropy of the charge density distribution and can be obtained directly from it. The theoretical results agree well with experimental EFGs.