s2.m1.o1 **DFT calculations on $KTiOPO_4$ (KTP) used in nonlinear optics.** K. Schwarz,[1] P. Blaha,[1] P. Delarue,[2] C. Lecomte,[2] V. Jennings,[3] P.A. Thomas,[3] *[1]Technische Universität Wien, A-1060 Vienna, Austria, [2]Université Henri Poincaré F-54506 Nancy, France, [3]University of Warwick, Coventry, CV4 7AL, UK*.
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Density functional theory (DFT) is a powerful quantum mechanical scheme in which exchange and correlation effects are treated in an efficient but approximate way. Modern versions on the basis of the generalized gradient approximation (GGA) have reached high accuracy.

One of the most accurate schemes to solve the DFT equations is the linearized augmented plane wave (LAPW) method, embodied in the WIEN code that has been developed in our group during the last 20 years.[1] It is used worldwide by about 400 groups and allows one to calculate many properties that are important in material science. These quantities include the band structure, densities-of-states, electron (or spin) densities, charge distributions, electric field gradients, partial charges, total energies, forces acting on the atoms (for structure optimization), x-ray and optical spectra, etc.

The potential of such DFT calculations is illustrated for potassium titanium oxide phosphate, $KTiOPO_4$ (KTP) that is a well known material used in nonlinear optics (NLO).[2] Its chemical and thermal stability as its other properties make it very interesting for different applications, for example, optical frequency conversion, second-harmonic generation (SHG), optical parametric amplification, optical parametric oscillation and manufacturing optical wave-guides.

The KTP structure is very versatile with respect to isomorphous substitution.[2] The potassium cation can be replaced (totally, partially or not at all) by Rb^+ (or Na^+, Tl^+, Cs^+, Ag^+ and $NH4^+$) whereas arsenic atoms may replace some of the phosphorus atoms (also the titanium center may be substituted by Ge^{4+}, Sn^{4+} and Zr^{4+} cations). Solid solutions[3] exist between many of these species, allowing the possibility of selective modification of the non-linear optical properties.

Although KTP contains 64 atoms per unit cell (space group Pna21) and is non centrosymmetric, it was possible to perform DFT calculations using WIEN97[1] and a powerful vector computer (NEC SX4) with a large memory (2Gb). A comparison between the theoretical and experimental electron density provides a first insight into the chemical bonding in the regions that are crucial for NLO. DFT calculations may help to move from a trial and error scheme to a systematic search for the optimal composition once the correlations between the optical non-linearities (measured as SHG) and the structural distortions are understood.

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s2.m1.o2 **Experimental charge densities of novel thermoelectric clathrate materials.** B.B. Iversen, *Department of Chemistry, University of Aarhus, Denmark*
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Thermoelectricity is a unique phenomenon of energy conversion suitable for power generation and cooling applications. In an ongoing search for improved thermoelectric materials we are studying clathrate framework structures[1-3]. These materials constitute some of the most promising non-optimized structures discovered so far for thermoelectric applications. Due to the compositions of known clathrates there is a general belief that the guest atoms donate valence electrons to the framework. The detailed nature of the host-guest interactions, the defect chemistry and thermal motion of the guest atoms are all properties of great importance for the material performance. Crystallographic methods are well suited for studying such properties.

Theoretical calculations surprisingly show that the Sr guest atoms in $Sr_8Ga_{16}Ge_{30}$ appear neutral[4]. In order to validate this suggestion we have used accurate single crystal X-ray diffraction and X-ray absorption spectroscopy to study the charge distribution in $Sr_8Ga_{16}Ge_{30}$ as well as in a number of other clathrate type I structures. Using some novel approaches to analysis of Maximum Entropy Method (MEM) electron densities we have shown[3] that the strontium structure in fact contains guest atoms of mixed valence. Mixed valence systems are well known among transition metal complexes, but very unusual for alkali or alkaline earth metals. The MEM approach has shown itself to be particularly useful in studies of disordered systems like $Sr_8Ga_{16}Ge_{30}$, where conventional multipole modeling fails. Multipole modeling is on the other hand very useful in studies of ordered structures. One such example is $Rb_{7.3}Na_{16}Si_{136}$, where extremely extensive single crystal data have been collected using synchotron radiation ($(\sin\theta/\lambda)max = 2.01$ Å^{-1}). The data were modeled with the XD program.

Other work concerns determination of the nuclear density distribution in $Ba_8Ga_{16}Si_{30}$ based on multitemperature (15, 100, 150, 200, 250, 300, 450, 600, 900 K) single crystal neutron diffraction studies. The data allows examination of anharmonic motion using both direct and reciprocal space fitting techniques. The thermal motion of the atoms can furthermore be used to estimate the lattice contribution to the thermal conductivity[5].

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