P.14.02.1
Acta Cryst. (2005). A**61**, C421

Advances in Charge Density and Electrostatic Interaction Analyses

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The number of high resolution biological macromolecules X-ray structures increases regularly. Feasibility of multipolar refinement of protein structures has been proved [1, 2], assuming subatomic resolution and sufficiently low thermal motion. The high resolution crystallographic refinement program MoPro employs a multipolar representation of the electron density, the latest functionalities will be described [3,4].

Electrostatic properties are of major importance in numerous biological and molecular recognition. Three methods are employed in the VMoPro software to calculate the accurate electrostatic potential and the interaction energy:
* numerical grid integration
* Buckingham summation of charges & multipoles interaction
* coulombic energy using real and virtual spherical atoms.

The electron density parameters are obtained either from a crystallographic refinement or from a database transfer [5]. The applications go from small compounds crystals to protein–ligand complexes.

[1] Muzet N., Guillot B., Jelsch C., Howard E., Lecomte C., *PNAS*, 2003, **100**, 8742. [2] Jelsch C., Teeter M.M., Lamzin V., Pichon-Pesme V., Blessing R.H., Lecomte C., *PNAS*, 2000, **97**, 3171-3176. [3] Jelsch C., Guillot B., Lagoutte A., Lecomte C., *J. Appl. Cryst.* A, 2005, **38**, 38-54. [4] Guillot B., Viry L., Guillot R., Lecomte C., Jelsch C., *J. Appl. Cryst.*, 2001, **34**, 214. [5] Pichon-Pesme V., Jelsch C., Guillot B., Lecomte C., *Acta Cryst.*, 2004, **A60**, 204-208.
Keywords: charge density, protein, database

P.14.03.1
Acta Cryst. (2005). A**61**, C421

Bond-dependent Crystal Response on Electric Field: Synchrotron Diffraction Study

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The interaction of a crystal with the permanent external electric field resulting in dielectric polarization and converse piezoelectric effect is well described on the macroscopic level. In last years the microscopic origin of these phenomena is actively studied by means of synchrotron diffraction technique. In this work, we present our recent investigations of the structural response of single crystals to an external electric field, and analyse the results in terms of the chemical bond in different structural units of the crystal.

Special attention will be paid to the study of bond specific structural response in α-GaPO$_4$. The experiment was carried out by modulation-demodulation technique at D3 beamline at HASYLAB. The measured diffraction intensities of 42 independent reflections were fitted to a structural model, validated on the basics of the developed theory of X-ray diffraction by a crystal in the external electric field [1]. The difference of field-induced deformations of GaO$_4$ and PO$_4$ tetrahedra is explained in terms of the different character of chemical bonds and by charge density features. Support by DFG and A.v.Humboldt-Foundation (V.T.) is kindly acknowledged.

[1] Gorfman S., Tsirelson V., Pietsch U., *Acta Cryst.*, 2005, **A**, *submitted*.
Keywords: X-ray diffraction, dielectric properties, chemical bonding

P.14.03.2
Acta Cryst. (2005). A**61**, C421

Electron Density Analysis of Borocarbides

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Quaternary rare earth nickel borocarbides, space group (139) *I4/mmm*, exhibit different low temperature properties [1,2]. Only superconductivity at temperatures of about 8 K is observed for R = Y, Lu. For R = Ho additional magnetic ordering occurs in the range of 4 to 6 K whereas superconductivity is destroyed. Further cooling leads to superconductivity again which is the so called re-entrant behaviour. This depends strongly on the crystal composition within the small homogeneity range and the thermal treatment after crystal growth.

Single crystals of compositions mentioned above were investigated by means of single crystal diffraction methods using both X-ray tubes and high energy synchrotron radiation sources under ambient conditions. Structure refinement and Fourier Difference Analysis of the experimental data were performed to determine small influences of chemical and structural disorder.

Experimentally determined electron densities are compared with theoretical calculations.

[1] Nagarajan R., Mazumdar C., Hossain Z., Dhar S.K., Gopalakrishnan K.V., Gupta L.C., Godard C., Padalia B.D., Vijayaraghavan R., *Phys. Rev. Lett.*, 1994, **72**, 274. [2] Siegrist T., Cava R.J., Krajewski J.J., Peck W.F., J. *Alloys Compd.*, 1994, **216**, 135.
Keywords: rare-earth, superconductivity, electron density

P.14.03.3
Acta Cryst. (2005). A**61**, C421

Chemical Bonding and Electronic Configuration of Nitrosyl Iron Complexes

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The nitrosyl non-heme iron complexes with sulfur ligands are extensively synthesized to study the interaction of NO and iron-sulfur protein. In this report, the electron density distribution of mono- and di-nitrosyl iron sulfur compounds are studied with multipole model based on X-ray diffraction data. In the dinitrosyl iron complexes (DNIC), the coordination sphere of Fe is a tetrahedral Fe(NO)$_2$(S)$_2$ core such as [S$_5$Fe(NO)$_2$]$^-$ and [Fe(NO)$_2$(SR)$_2$]$^{-1/0}$. In five-coordinated complexes, it turns out to be a tetragonal pyramidal Fe(NO)(S)$_4$ geometry for mononitrosyl complexes such as [(NO)Fe(S, S-C$_6$H$_4$)$_2$]$^{-1/-2}$and Fe$_3$(NO)$_3$(S, S-C$_6$H$_4$)$_3$. To illustrate the bonding character, the topological properties associated with the bond critical points (BCP), Laplacian of the electron density as well as electron density at the BCP of each chemical bond will be presented. The comparison between experiment and theory will be made. Because of the ambiguity of the traditional way to discriminate the oxidation states of NO, NO$^+$ and NO$^-$ group by bond angles and vibrational frequency, the X-ray absorption spectroscopy of Fe K-, L-edge and N/O/S K-edge are used to investigate the oxidation state of metal, NO groups and sulfur lignads. Moreover, the magnetic susceptibility and electron paramagnetic resonance results will be included to illustrate the electronic configuration among Fe and NO groups. Based on the Enemark-Feltham notation, all results toward the conclusion that the best way to describe the present dinitrosyl and mononitrosyl cases are {Fe^{+1}(•NO)$_2$}^{9} and {Fe^{+1}(NO^{+1}) }^{7}.

Keywords: nitrosyl, BCP, X-ray absorption spectroscopy

P.14.03.4
Acta Cryst. (2005). A**61**, C421-C422

Pump and Probe the Structure and Electronic Configuration of LIESST State

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A six-coordinated iron(II) complex, t-Fe(tzpy)$_2$(NCS)$_2$ (tzpy = 3-(2-pyridyl)[1,2,3]triazolo[1,5-a]pyridine), undergoes a graduate spin transition from a paramagnetic high spin state ($^5T_2$, S = 2, HS-1) above 200K to a diamagnetic low spin state ($^1A_1$, S = 0, LS-1) below 75 K according to the magnetic measurement. The crystal structures of both HS-1 and LS-1 are studied at 298 and 40K respectively. Significant differences in Fe-N distances and in coordination geometries of Fe do occur during the spin transition. The electronic configuration of Fe in both HS and LS states is monitored by Fe K- & L-edge absorption. In addition, the ligand C-N stretching frequency can also be followed through the spin transition.

A light-induced-excited-spin-state-trapping phenomenon (LIESST) is observed by pumping the crystal with 532nm laser at 40K, where a relatively long-lived high spin state (HS-2) occurred. The molecular and crystal structure of this HS-2 state is investigated using pump and probe mode. The excitation can be easily detected by XRD, XAS and IR spectroscopy. The molecular structure and electronic configuration of Fe of HS-2 state are very similar to those of HS-1. The relaxation from such HS-2 state to the low spin state (LS-2) is followed via C-N stretching frequency at various temperature.

Keywords: spin-crossover, X-ray absorption spectroscopy, excited spin state

P.14.04.1

Structure Refinements of Protein-ligand Complex by the Maximum Entropy Method

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It is important to have detailed structural information of protein crystal to understand functions of a protein. Particularly, interaction between protein and ligand molecule is a fundamental aspect of protein crystallography. The experimental techniques of protein crystallography have been very rapidly improved due to, for example, advent of Synchrotron Radiation source. Hence, it becomes rather usual to collect fairly good quality data set for a protein crystal. The analytical techniques for structure determination of protein crystals have also drastically improved. However, the structure refinement method still remains in an old fashion, i. e. Fourier method.

For materials with simple structure, more sophisticated method called the Maximum Entropy Method (MEM)[1] is now commonly used to obtain accurate electron density distributions. In order to demonstrate the ability of MEM for structure refinement in protein crystallography, the complex of ribose-5-phosphate isomerase(Rpi)[2] between both ribose 5-phosphate(R5P) and arabinose-5-phosphate (A5P) are refined by MEM. Isomerization to ribulose-5-phosphate proceed only for R5P but not for A5P. The MEM density maps revealed very clearly the structural differences between Rpi/R5P and Rpi/A5P.

[1] Sakata M., Sato M., *Acta Cryst.*, 1990, **A46**, 263. [2] Hamada K. *et al.*, *J. Biol. Chem.*, 2003, **278**(49), 49183.

Keywords: protein structure refinement, maximum entropy method, Rpi

P.14.04.2

Maximum Entropy and Fourier Study on Electron Density of MnO, LaCoO$_3$ and MgSiO$_3$

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The maximum entropy method (MEM) gives us the deduced electron-density distribution without the use of any structure model [1]. On the other hands, the difference-Fourier (D-FR) method is well known to estimate the accurate electron-density through the Fourier transform. We have examined the validity to apply the MEM for electron-density studies in physically meaningful and relatively complicated structures. In this study, the MEM and D-FR maps derived from single-crystal X-ray diffraction data were compared for three materials, i.e. MnO, LaCoO$_3$ and MgSiO$_3$, after optimizing MEM parameters such as resolution and constraint condition.

MnO gave the anisotropic distribution of Mn 3*d*-electrons in the NaCl structure, although Mn^{2+} ions should be spherically distributed in the regular-octahedral coordination. LaCoO$_3$ has a maximum of susceptibility in the temperature range of 100 K, where Co^{3+} ions may have an intermediated spin-state. The temperature dependence of electron density was examined in this study. In a chain of SiO$_4$ tetrahedra in MgSiO$_3$, two Si-O bridging bonds and the other two non-bridging bonds had different covalent characters. It is conclusive that electron-density distributions deduced by the MEM are well compared with those estimated from the D-FR calculation.

[1] Sakata M., Sato M., *Acta Crystallogr.*, 1990, **A46**, 263.

Keywords: maximum-entropy method, Fourier methods, electron density distribution

P.14.05.1

Electron Density in Cubic SrTiO$_3$ from γ–ray Diffraction

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The electron density and atomic displacements in the prototype perovskite SrTiO$_3$ have been studied using extensive and accurate γ-ray diffraction data (λ = 0.0392 Å) at room temperature. The 6 strongest structure factors have been determined under extinction-free conditions by means of an extended-face thin-crystal plate in Laue geometry, so that the lowest I_{obs}/I_{kin} ratio was 0.98 for the full data set. The maximum thermal diffuse scattering contribution was only 3% at $\sin\theta/\lambda = 1.72$ Å^{-1}.

The thermal displacement parameters are in good agreement with lattice dynamical calculations as well as with neutron diffraction results. Contrary to simple expectation, anharmonic motion effects are negligible for all atoms. This finding is consistent with a previous γ-ray study which revealed SrTiO$_3$ as a harmonic system at $T_c + 5$ K [1], *i.e.* very close to the antiferrodistortive phase transition.

The charge density was modeled using *VALRAY*. The population of the 3*d* subshell on Ti is found to be 0.200(45) |e|, *i.e.* close to zero, in agreement with the observed magnetic behaviour. The electronic properties at the bond critical points indicate ionic Ti-O and Sr-O interactions of different strength which is corroborated by the net charges of the atomic basins: q(Sr) = 1.18 |e|, q(Ti) = 3.10 |e| and q(O) = −1.42 |e|.

[1] Jauch W., Palmer A., *Phys. Rev. B*, 1999, **60**, 590.

Keywords: γ-ray diffraction, charge density inorganic compounds, perovskite oxides

P.14.05.2

High-resolution Magnetic Compton Profile of Iron

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A high-resolution magnetic Compton profile of ferromagnetic iron was measured with a momentum resolution of 0.14 atomic units. The results are compared with those obtained by FLAPW calculations [1].

Most of the magnetic Compton experiments have been performed with an energy dispersive spectrometer using a solid-state detector. With such detectors it is impossible to achieve a momentum resolution better than Δp ~ 0.4 atomic units. With a wavelength dispersive spectrometer, a higher resolution measurement can be performed. However, it usually takes a couple of weeks to acquire significant data