

MS09.01.05 THE PRIOR IN THE MAXIMUM ENTROPY METHOD. DO NON-NUCLEAR MAXIMA IN BE AND SI EXIST? R. Y. de Vries, W. J. Briels & D. Feil, Chem Phys. Lab. University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

In the past few years the maximum entropy method (MEM) has become very popular for extracting electron density distributions (EDD) from X-ray diffraction data. In the MEM formalism, the EDD is described on a very dense grid. It is believed that, in contrast to multipolar refinement, the MEM is 'model free'.

The discovery by the MEM of maxima in the EDD that are not located at a nucleus, the non-nuclear maxima, in Si and Be could be the result of this enormous flexibility. On the other hand, these non-nuclear maxima could also be an artifact of the MEM.

We have tested the MEM on data calculated from a known EDD of silicon. This EDD was calculated with the Amsterdam Density Functional-BAND program which takes the periodicity of the crystal into account. No non-nuclear maxima were observed in this density. When the MEM was applied on the structure factors calculated from this density non-nuclear maxima appeared in the Si-Si bond. This clearly demonstrates that these maxima in Si are an artifact of the MEM.

The MEM as used above strives towards an EDD displaying as few features as possible within the constraints given by the experiment. We know, however, that our EDDs are characterized by sharp atomic peaks. By including this prior knowledge in the form of the sum of the free atoms, the MEM gave an excellent reconstruction of the EDD. Applying this to the experimental data of both Si and Be did not reveal any non-nuclear maxima. These EDDs will be compared with the EDDs resulting from multipolar refinements.

MS09.01.06 A BAYESIAN APPROACH TO HIGH-RESOLUTION X-RAY CRYSTALLOGRAPHY: ACCURATE DENSITY STUDIES WITH PROGRAM BUSTER. Pietro Roversi, Dipartimento di Chimica Fisica ed Elettrochimica, Università di Milano, Via Golgi 19, 20133 Milano, Italy; John Irwin and Gérard Bricogne, MRC-LMB, Hills Road, CB2 2QH, Cambridge, England, UK

Implementation around the existing code BUSTER [1] of algorithms to perform accurate electron density studies from high-resolution X-ray diffraction data has been accomplished, as part of a comprehensive programme for doing crystallography within a Bayesian theory of structure determination [2]. We consider the reconstruction of an accurate electron density as an extension of the structure determination process. The program seeks the electron distribution having maximum entropy relative to a given prior, and reproducing the experimental measurements. The program is fully automated, space-group general and is operated from a user-friendly graphical interface. The maximum-entropy equations are solved by means of a robust and efficient algorithm, targeting phased structure factors values. An interface between BUSTER and the program for multipolar electron density studies VALRAY [3] allows one to define a 'fragment' of atomic core density functions, and to redistribute only the valence electrons. A prior distribution for the latter can be computed within VALRAY from a superposition of atomic valence density functions and is used to provide a description of the radial dependence of the atomic density, thus preventing the accumulation of density in regions far from the nuclei within the crystal.

First tests against synthetic data have confirmed the viability of the method to obtain dynamic densities for centrosymmetric structures (Si, Be, TriGlycine). Non-centrosymmetric crystals, which present the added difficulty of phase uncertainty, have also been studied. We are still investigating the dependence of the final

reconstructed densities on the choices made for the prior, and comparing them with the traditional multipolar densities. There is strong evidence of the need to use a thermally smeared prior density.

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PS09.01.07 DIFFUSE SCATTERING ACCOUNT IN ACCURATE DIFFRACTION STUDIES: A PRACTICAL APPLICATION A. I. Stash*, V. E. Zavodnik*, V. G. Tsirelson#, D. Feil\$, *Karpov Institute of Physical Chemistry, Moscow, Russia, #Mendeleev University of Chemical Technology, Moscow, Russia, \$University of Twente, Enschede, the Netherlands

Diffuse scattering (dynamic and static) contribution in diffraction intensities influences both thermal atomic parameters and electron density maps. It depends on concentration of defects contributing to scattering near Bragg position of the peak in the reciprocal space and is increased when temperature of the experiment is close to phase transition point. The experimental method of the diffuse scattering account was suggested in [1]. We are presenting in this report the application of this method for studying of a few organic and inorganic compounds at different temperatures and for samples of quartz with different defect structures. The anisotropy of thermal diffuse scattering was found in the hexahydroquinolone crystals at room temperature and its increasing when temperature approached to phase transition point at 248 K.

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PS09.01.08 IS THE COMBINATION OF FAST, HIPPO, DREAM AND XD THE NEW WAY FORWARD TO CHARGE DENSITY ANALYSES? Bracke, Ben R. F. and Hursthouse, M. B. University of Wales Cardiff, Chemistry Department, P.C. Box 912, Cardiff CF1 3TB, UK.

The use of Area Detectors has become widespread in recent years and their applications both in X-ray and neutron diffraction show exciting results. An area in which its use to date has been far from routine so far is in the area of multipole refinement in order to obtain charge, spin and momentum density properties of the investigated compound.

The main problem until recently has been the way the area detector data are processed. Most commercial data collection packages provided with the diffractometer, including our FAST software, use an algorithm that assumes a priori knowledge of the peak shape which is in most cases based on an elliptical peak mask (Wilkinson et al., 1983; Kabsch, 1988a, 1988b).

Recently, a new method of area-detector peak integration - the 'Seed-Skewness Method' (Bolotovskiy et al., 1995) has been developed (and implemented in the program HIPPO) in which the integration is purely based on the statistical analysis of pixel intensities and hence uses no a priori knowledge of the peak. According to the first results mentioned in their article, it gives much better and more reliable results especially for the weak reflections, takes care of the α_1/α_2 separation and shows no significant difference in positional and thermal parameters after standard spherical atom refinements compared to data obtained via the earlier mentioned peak mask methods.

This observation was promising enough to start implementing this new Seed-Skewness method in our data collection procedure. By making use of the well established data reduction package

DREAM (Blessing, 1986) and the recently developed multipole refinement and analyses package XD (Koritsanzsky et al., 1994), we will present charge density analyses results on Creatine Monohydrate using both the Seed-Skewness method and the elliptical peak-mask method.

An interactive version of this abstract can be obtained from the URL: <http://www.cf.ac.uk/uwcc/chem/bracke/iucr/iucr96.html>

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PS09.01.09 ANHARMONICITY IN MnF_2 AT LOW TEMPERATURE: BEYOND THE FROZEN-CORE APPROXIMATION. By W. Jauch, Hahn-Meitner-Institut Berlin, Germany, A. J. Schultz, Argonne National Laboratory, IL, USA, R. F. Stewart, Carnegie-Mellon University, Pittsburgh, PA, USA

Antiferromagnetic order in MnF_2 induces a dipolar distortion of the fluorine inner electron shell. The core-deformation generates a substantial electric field at the nucleus, which is not compensated by peripheral lattice contributions, thus giving rise to an apparent Coulomb force on the nucleus. The force exerted on any nucleus should vanish in the stable equilibrium configuration. A local source of an opposing electric field could consist in a small skewness of the fluorine nuclear vibrational distribution which should persist even in the limit of zero temperature. This model rests upon the assumption that the electron deformation does not rigidly follow the nuclear motion.

Pulsed single-crystal neutron diffraction ($T = 15$ K) at the spallation source IPNS has been used to test this hypothesis. Data have been collected up to very high diffraction vectors, $(\sin\theta/\lambda)_{\max} = 2.75 \text{ \AA}^{-1}$. The harmonic mean-square displacement parameters are in excellent agreement with previous results from both gamma-ray and neutron diffraction. Statistically significant third-order coefficients of a Gram-Charlier expansion could be extracted from the experiment. The shape of the antisymmetric part of the nuclear distribution function substantiates a subtle balance between the mean thermal electric fields due to the electronic and the nuclear charge density distribution. The sense of the skewness around the equilibrium position is opposite to the one found previously for the paramagnetic state. It is to be noted that data from nuclear scattering alone can provide valuable indications concerning a local redistribution of electron density.

Experiment thus confirms the conclusion that the core polarization in antiferromagnetic MnF_2 is dynamically stabilized. A theoretical description of the detailed physical mechanism is lacking at present.

PS09.01.10 ELECTRON DENSITY AND PROPERTIES OF ROCK-SALT TYPE CRYSTALS V. E. Zavodnik*, Yu. A. Abramov#, A. I. Stash*, E. L. Belokoneva%, A. S. Avilov**, U. Pietsch, J. Stahn, & D. Feil^S, V. G. Tsirelson#, *Karpov Institute of Physical Chemistry, Moscow, Russia; #Mendeleev University of Chemical Technology, Moscow, Russia; %Moscow State University, Moscow, Russia; **Institute of Crystallography, Moscow, Russia, & Potsdam University, Potsdam, Germany; ^STwente University, Enschede, the Netherlands.

The X-ray diffraction studies of the electron density (ED) of the crystals with rock-salt structure, traditional test crystals in solid state computational methods, should provide the basis for direct comparison of the theoretical and experimental data. However,

the severe extinction and sometimes ignoring TDS distort the diffraction intensities and the problem of description of highly ionic electronic states exists in theoretical calculations for these crystals. Therefore the reliable estimation of real today's level of both experimental and theoretical results concerned with electronic properties of these crystals is needed.

We have performed the accurate X-ray diffraction experiments and theoretical calculations by non-empirical Hartree-Fock method for LiF, NaF, NaCl and MgO crystals. In addition, the electron diffraction measurement of electrostatic potential in MgO was done. The quasi-static structure amplitudes reconstructed from the X-ray experiments were compared with theoretical ones calculated with different basis sets at experimental geometry. It was found that the extended optimised basis sets result to close agreement with experimental data, including low-angle "extinctional" reflections. The analysis of the ED (both experimental and theoretical) in terms of deformation density maps and Bader's quantum-topological theory was done. The electrostatic potential was calculated and compared with electron-diffraction data.

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PS09.01.11 CHARGE DENSITY STUDIES OF TRANSITION METAL SULFIDES. Zhengwei Su and Philip Coppens (Chemistry Department, State University of New York at Buffalo, Buffalo, NY 14260) Nobuo Ishizawa (Tokyo Institute of Technology, Yokohama 226, Japan) and Natalie Holzwarth and Yueping Zeng (Physics Department, Wake Forest University, Winston-Salem, NC 27109).

The electron density distributions of transition metal sulfides MS_2 (pyrite structure) for $M = Mn, Fe, Co,$ and Ni have been analyzed by multipole refinement and topological analysis using the XD program package (1), with data reported previously (2). The metal d-orbital populations and deformation density maps confirm that the transition metal in MnS_2 is in a high spin state, while low spin states occur in the other solids. The electron density at the M-S bond critical points decreases as the bond length increases, indicating decreasing bond strength. The Laplacians at the S-S and M-S bond critical points are all positive. Their values do not correlate well with the bond lengths or densities. The structure factors from a theoretical DFT calculation on FeS_2 (3), have been analyzed with the multipole formalism. Experimental and theoretical multipole parameters and density maps will be compared.

The effect of the use of selection of different form factors (non-relativistic, relativistic and modified relativistic) will be discussed.

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