IUCr COMMISSION NEWS

Contributions intended for this section should be submitted to The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

COMMISSION ON CHARGE, SPIN AND MOMENTUM DENSITIES

Acta Cryst. (1990). A46, *FC1–FC4*

Newsletter No. 2

This second newsletter includes reports on the Gordon Conference on Electron Distributions and Chemical Bonding and on the Postsymposium at the 12th European Crystallographic Meeting in Moscow on Chemical Bonding and Lattice Dynamics in Crystals and Molecules. We also report on the present state of planning for Sagamore X, which is to be held in Konstanz in 1991, and on invitations for Sagamore XI in 1994.

E. N. Maslen, D. Feil and K. Hermansson present their ideas on a Commission project on 'Evaluation and/or measurement of the electron density in perovskite structures'. W. Weyrich and V. H. Smith suggest a Commission project on 'Quantum mechanical description of electronic structure from experimental charge and momentum densities'. All authors would be happy to receive further suggestions, which will be considered before the Commission decides on the project next summer in Bordeaux.

The Commission have suggested two Microsymposia and an Open Commission Meeting for the IUCr XV Congress in Bordeaux in 1990. The proposed subjects interest a wider community of crystallographers and have been accepted by the Programme Committee. Everybody is invited to contact the Chairpersons of these sessions with suggestions and/or criticisms. It is desirable that a reasonable number of posters related to the topics of these Microsymposia and the Open Commission Meeting are submitted, so that thorough discussions on special aspects of the subjects can complement the sessions.

Gordon Conference on Electron Distribution and Chemical Bonding

According to the rules of Gordon Research Conferences only the names of the invited speakers and the titles of their contributions are listed.

Applications of synchrotron radiation (P. Coppens, Buffalo, USA; M. Cooper, Warwick, UK)

G. Lander (Karlsruhe, FRG): *Diffraction studies of bonding involving 5f electrons.*

Å. Kvick (Brookhaven, USA): *Perturbation of the charge density in an applied field.*

A. Kirfel (Saarbrucken, FRG): *Accurate structure analysis using synchrotron radiation.*

N. Sakai (Photon Factory, Japan): *High resolution measurement of Compton profiles.*

S. Manninen (Helsinki, Finland): *Momentum densities.*

Charge density and the theory of chemical bonding (R. Messmer, General Electric, USA; M. Newton, Brookhaven, USA)

M. Levy (Tulane, USA): *Density functional theory.*

W. Kutzelnigg (Bochum, FRG) *IGLO calculations of current densities and properties of molecules in magnetic fields.*

W. Goddard (Caltech, USA): *Generalised valence bond theory.*

P. Schultz (Sandia, USA): *Theoretical studies of multiple bonds.*

Panel: M. Newton, M. Levy, W. Goddard, W. Kutzelnigg, R. Bader, K. Ruedenberg.

Electrostatic properties from diffraction and theory (R. Stewart, Carnegie-Mellon, USA; R. Bader, McMaster, Canada)

J. Spence (Arizona, USA): *Accurate structure factor refinement and phase measurement in noncentrosymmetric microcrystals by convergent beam electron diffraction.*

J. Dows (Ohio, USA): *Charge density in* BeO *and quartz.*

R. Destro (Milan, Italy): *H-bonded crystal structures.*

M. Spackman (Armidale, Australia): *Electric and magnetic properties of molecules in crystals.*

K. Ruedenberg (Iowa, USA): *Atomic groundstate orientations, chemical difference densities and chemical binding.*

Studies of chemical bonding (J. R. Schneider, Berlin, FRG; P. Becker, Paris, France)

W. Klemperer (Illinois, USA): *Charge distribution and reactivity of metal-oxide clusters.*

R. Smalley (Rice, USA): *Let's think about* Si_{39}^+.

J. Dye (Michigan State, USA): *Electron localisation in electrides.*

W. Jauch (Berlin, FRG): *Manganous fluoride.*

Panel: P. Becker, D. Feil, E. N. Maslen, R. Stewart, M. Cooper, E. D. Stevens, J. R. Schneider.

Charge and spin densities in superconducting oxides (E. D. Stevens, Tulane, USA)

J. Jorgensen (Argonne, USA): *Structural studies of doping and charge transfer mechanisms in oxide high-T_c superconductors.*

S. Sinha (Exxon, USA): *Charge density in high T_c compounds.*

E. Mele (Penn, USA): *Theoretical approaches to oxide superconductors.*

Symposium on Chemical Bonding and Lattice Dynamics in Crystals and Molecules

Fourteen invited talks and 42 posters (mainly from the USSR) were presented at the two-day Symposium at the 12th ECM. In order to give an impression of the scope of the meeting, the invited speakers and the title of their presentations are listed:

R. F. W. Bader: *Atoms in molecules – a quantum theory.*

J. D. Dunitz: *Atomic motion in molecular crystals. What can one learn from diffraction studies.*

V. G. Tsirel'son: *Electron density and crystal properties.*

H. B. Bürgi: *Empirical potential energy surfaces relating ground state structure, transition state structure and activation energy.*

V. S. Urusov: *Electron density distribution in oxides, phosphates and silicates: the experimental data analysis.*

G. J. McIntyre, H. Ptasiewicz-Bak, I. Olovsson: *Partitioning of weak bonding interaction in tetragonal* $NiSO_4.6D_2O$.

M. Yu. Antipin, Yu. T. Struchkov: *Electron density distribution and diversity chemical bonds of different types in the crystals of organoelement compounds.*

R. Bianchi, C. M. Gramaccioli, T. Pilati: *An extension of Bertaut method for evaluating lattice sums for dynamical calculations.*

R. Bianchi, R. Destro, F. Merati: *Electrostatic properties of syn-1.6:8.13-biscarbonyl[14]-annulene.*

R. A. Evarestov, V. P. Smirnov: *Band corepresentation of magnetic space groups.*

S. Gehring, W. Haase: *Mixed-bridged copper(II)-trimers with ferromagnetic ground states: structures, magnetic properties and ESR spectra.*

F. L. Hirshfeld: *Recent experiences with multipole refinements of molecular deformation densities.*

J. Leciejewicz, A. Szutula: *Magnetic ordering in MT_2X_2 compounds.*

V. A. Strel'tsov, V. G. Tsirel'son, R. P. Ozerov, K. Yvon: *The 3d-orbital population and cation–cation interactions in 3d-metal sesquioxides studied by X-ray diffraction.*

Proposal for a Commission project on evaluation and/or measurement of the electron density in perovskite structures

The D-(+)-tartaric acid project in 1970 assessed the accuracy of measured structure factors. The oxalic acid dihydrate project in 1984 focused on the electron density in a molecular crystal composed of first-row atoms. The new project will test accurate studies of lattice-type structures containing heavier atoms.

The materials selected for analysis are the perovskite family. The ideal members have composition ABX_3, and cubic $Pm3m$ symmetry, with A atoms at each corner of the cubic cell, a B atom at 1/2, 1/2, 1/2 and an X atom at the midpoint of each cell edge. Nonideal members approximate that composition and/or symmetry. For the purposes of the project the perovskite family will be interpreted broadly, to include the related K_2NiF_4 and K_2PtCl_6 structures.

The series includes technologically important compounds such as $SrTiO_3$ and $BaTiO_3$ (used in optoelectronics), $YBa_2CuO_{7-\delta}$ (a high-temperature superconductor), $LiNbO_3$ (a ferroelectric material used in high-density digital memories).

The project involves the measurement and/or prediction of the properties, such as structure factors, related directly to the electron density in perovskites. This includes the distribution function for the nuclei which can be inferred. An important characteristic of the perovskite family is the number and variety of the phase transitions for many of its members. The project provides an opportunity for studying properties of the density related to those phase transitions.

The methodology differs from that of previous projects, in so far as participants are free to select any member of the series for analysis. However,

participants should calibrate their calculations and/or measurements by reference to $KZnF_3$, the ideal cubic perovskite selected as a standard for this project. Large specimens can be grown from the melt. Small crystals are prepared by slowly mixing KF and $Zn(NO_3)_2$ solutions.

In setting up theoretical calculations it should be noted that experimental difference densities for perovskite structures contain significant density, often resembling ghost atoms near the structural holes at the centres of the faces of the cube. These are more than 2Å from the nuclei of the nearest atoms, and the electron difference density at these sites is a sensitive function of the cell size. It is hoped that the nature of these features in difference maps will be identified *via* this project.

Each investigator will be free to publish individual results following normal procedures and standards for publication, but should forward copies of their data and conclusions to one of the project coordinators:

E. N. Maslen, Crystallography Centre, University of Western Australia, Nedlands, Western Australia 6009, Australia

D. Feil, Chemical Physics Laboratory, Twente University of Technology, PO Box 217, 7500 AE Enschede, The Netherlands

Kersti Hermansson, Institute of Chemistry, Uppsala University, Box 531, S-75121 Uppsala, Sweden

Additional information can be obtained from E. N. Maslen, who will supply small crystals of $KZnF_3$ on request.

Proposal for a Commission project on quantum mechanical description of electronic structure from experimental charge and momentum densities

Given the wavefunction of a quantum system, all observables can be calculated, whereas the calculation of wavefunctions from observables has seemed to be impossible or even forbidden. As a consequence, experimentalists generally measure various observables, theoreticians calculate (model) wavefunctions, and both compare the results. Since wavefunctions enter different observables in different ways, it is often difficult to understand the origin of discrepancies between theory and experiment. It is therefore an old goal (W. Pauli, 1933) to find a general method to derive the wavefunctions from observables.

In 1969, Clinton, Galli & Massa introduced the idea of fitting electronic position-space densities by a first-order density matrix with the boundary condition of idempotency of the matrix in order to ensure compatibility with quantum mechanics. Since then the feasibility and the virtue of this approach has been demonstrated. More recently Weyrich & Schmider developed a technique to determine the first-order density matrix from charge and momentum density data. In terms of a LCAO description the position-space density will be chiefly used to fix the diagonal elements of the density matrix, whereas the momentum densities are mainly employed to fix the off-diagonal elements. This recent approach is not restricted to idempotent density matrices and is still quantum mechanically correct, *i.e.* it allows for electron correlation, atomic zero-point motion and thermal excitation; it converges faster by orders of magnitude and it shows completely transparent error propagation.

The techniques require further theoretical testing beyond beryllium, which is the most complicated case studied so far. The testing should include *p, d etc.* electrons, linear and nonlinear molecules, solids, open-shell systems (with nonzero spin densities and density matrices containing spin), spherical averages and directionally dependent data.

The next step will be to use real experimental data of the best possible reliability. This requirement is fulfilled in the case of silicon, for which such data already exist. With the availability of a new generation of Compton spectrometers at modern synchrotron-radiation sources the momentum density can now be measured with much higher resolution. In addition the calculated density matrices can be compared with those determined by inelastic scattering of standing wavefields in perfect crystals (Schülke & Mourikis, 1986).

Parallel to the silicon project all scientists interested in electron densities are also invited to provide accurate experimental data for other systems of interest, starting with systems of as low complexity as possible. Because of their predominance in diffraction work and their ability to provide three-dimensional data, solids will be the prime candidates.

People interested in such a project are invited to contact

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V. H. Smith Jr, Department of Chemistry, Queen's University, Kingston, Ontario K7L 3N6, Canada

XV IUCr Congress in Bordeaux, July 1990

Open Commission Meeting on Accuracy of Experimental Electron Densities

Chairperson: J. R. Schneider (Hahn-Meitner-Institut, Glienicker Str. 100, D-1000 Berlin 39, FRG)

A presentation of the accuracy of structure factors measured with modern laboratory based four-circle diffractometers followed by an analysis of the reliability of the values of physical quantities deduced from experimental charge density studies could open the session. The success of combining X-ray structure factors with neutron data and/or structure factors measured with synchrotron radiation could be discussed in the light of recent results. Finally, the state of the art in measuring highly accurate absolute structure factors using X-ray *Pendellösung* oscillations or convergent-beam electron diffraction could be reviewed.

Microsymposium on Extinction

Chairperson: N. Kato (Department of Physics, Meijo University, Tempaku-ku, Nagoya 468, Japan)

The session will start with a discussion of the success and the problems of the current approaches used for correcting diffraction data for extinction. However, it is suggested that the emphasis of the Microsymposium be on the presentation of the new concepts developed in the frame of the statistical dynamical theory, where the artificial distinction between primary and secondary extinction is overcome by a better understanding of the coherence of wavefields in imperfect single crystals. Comparison with experimental data will be made.

Microsymposium on Application of Charge Densities to Computer Simulation and Molecular Design

Chairperson: Kersti Hermansson (Institute of Chemistry, Uppsala University, Box 531, S-75121 Uppsala, Sweden)

Electron densities in simple materials can now be measured and calculated to a high degree of reliability. At the same time, equally dramatic advances have been made within computer simulation (molecular mechanics, Monte-Carlo and molecular dynamics) of more complex systems, typically in the pharmaceutical industry. Such calculations must, of necessity, involve gross oversimplifications. This provokes the immediate question: how can the detailed information derived from electron density studies be used to advantage in simulation work?

The topics covered by the invited speakers are planned to be: Computer modelling in drug design; Molecular dynamics simulation; Empirical potentials; Atomic charges from X-ray diffraction.

Contributions are invited from the fields of electron density studies, computer modelling and other pertinent areas.

Sagamore X in Konstanz, September 1991

The Conference will be held in Konstanz, FRG, 1–7 September 1991, either on the campus of the University with accommodation in hotels in the city of Konstanz or at a conference centre on the border of the lake Bodensee about 30 km from Konstanz.

The conference Chairman is Professor W. Weyrich, Fakultät für Chemie, Universität Konstanz, D-7750 Konstanz 1, FRG.

The Conference will be devoted to recent experimental and theoretical developments in the field of electron particle and spin distributions for studies of the electronic structure and chemical bonding of molecules and solids. Additionally, relations with other current research activities in Chemistry and Physics will be emphasized.

Comments and suggestions for the program are very welcome and should be directed to W. Weyrich.

Sagamore XI and XII

R. P. Ozerov informed the Commission Chairman that the Institute of Organic Chemistry of the Latvian Academy of Sciences is ready to invite the Sagamore Community to the USSR in order to hold Sagamore XI in Riga in 1994. The Conference site would be Jurmala, 20 km from Riga on the Baltic coast. Suggested dates for the conference are either the end of May or the end of August–beginning of September. Dr A. F. Mishnev from the Institute of Organic Chemistry of the Latvian Academy of Sciences would act as head of the local organizing committee. We are grateful for this kind offer and suggest that it be discussed in Bordeaux.

H. Nara, T. Kobayasi and F. Itoh from Sendai, Japan, offered to organize the 1997 Sagamore XII Conference in Japan.