

## 02-Methods for Structure Determination and Analysis, Computing and Graphics

dynamical effects and to increase the data set available for analysis a new approach has been implemented. The incident convergent beam of electrons is scanned in a cone of controlled angle and de-scanned below the specimen. For zone axis patterns, the circles of HOLZ reflections expand into annuli where the intensity within each CBED disc is integrated by rocking through the Bragg condition, as in X-ray diffractometers.

Another development, which we have been pursuing, involves the formation of coherent electron diffraction patterns from overlapping orders. With the probe slightly de-focused on the specimen the relative phases of overlapping orders may be determined directly from the fringe patterns formed in the regions of overlap. The de-focusing of the beam leads to a reduction of the beam damage which might otherwise occur. This method was first applied to various polytypes of SiC with phase determination of reflections in systematic rows parallel to the *c* axes. It has since been extended to cases of two and three-dimensional diffraction with overlapping orders. The limits to fringe visibility imposed by diffuse scattering has been overcome by energy-filtering the results using a Gatan imaging filter. The results are recorded by a CCD array and ethernet to an interactive graphics terminal for routine phase evaluation.

The phases measured are the relative phases of adjoining diffracted waves. In the case of crystals which are thin enough these phases are equal to those of the structure factors associated with the reflections. In general, however, dynamical diffraction theory is required to extract accurate structural information from the data. Fortunately, efficient routines are under development which should make this task straightforward. Computer simulations have already been generated as a function of specimen thickness to investigate the way in which dynamical phase changes enter into particular overlap regions.

**PS-02.04.08 STRUCTURE FACTOR DETERMINATION FROM ENERGY-FILTERED CBED PATTERNS.** By R. Høier<sup>1</sup>, R. Holmestad<sup>1</sup> and K. Marthinsen<sup>2</sup>, <sup>1</sup>Dept. of Physics, Univ. of Trondheim-NTH and <sup>2</sup>SINTEF Applied Physics, N-7034 Trondheim, Norway.

Based on the strong parameter dependencies that govern the complicated 2-D intensity distributions in convergent beam electron diffraction (CBED) disks, particularly in the non-systematic many-beam case, the present group has over the last years aimed at developing a general method for accurate determination of structure factor amplitudes and phases from CBED. It involves pixel by pixel comparisons between calculated and digitized experimental patterns and multiparameter minimalization of a fit index to a global minimum. In order to minimize necessary computer time the multiparameter minimalization is carried out through the use of conjugate gradient methods.

From a detailed study of the behaviour of the fit index near the global minimum for a 7-parameter minimalization in InP, an accuracy of approximately 1% seems achievable with unfiltered film based data.

The main factor which limits the accuracy is the diffuse background which appears in the experimental patterns, due to phonon, plasmon and single-electron excitations. This background is difficult to take properly care of in the simulations and can only be removed rather qualitatively and crudely from unfiltered data. This emphasize the need for energy filtered experimental intensities. In our laboratory 2-D energy filtered CBED patterns may be obtained in the 0-300 keV range with a modified PEELS system. The modification is so that besides normal operation the whole detector assembly may be rotated 90° about a horizontal axis. In this mode the diode array records a one-dimensional energy filtered line profile of

1024 pixels across the CBED disk. A 2-D energy filtered image is obtained by deflecting the CBED patterns across the spectrometer entrance slit, acquiring one line at a time. Relative to film registration this method strongly increases the accuracy of the input data for the structure parameter determination. Electron structure factor phases and amplitudes may be determined with a typical accuracy of less than 1° and 0.5%, respectively.

**PS-02.04.09 ELECTRON CRYSTALLOGRAPHY OF INORGANIC STRUCTURES AT 1Å RESOLUTION - A CHALLENGE TO X-RAY CRYSTALLOGRAPHY.** By X. D. Zou\* and S. Hovmöller, Structural Chemistry, Stockholm University, S-106 91 Stockholm, Sweden

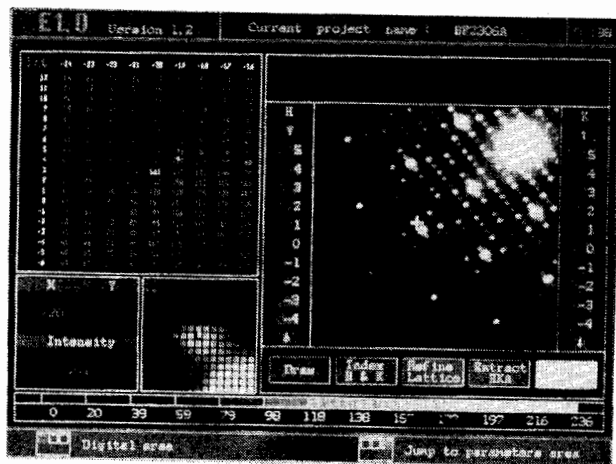
Electron crystallography is a technique for determining crystal structures from high resolution electron microscopy (HREM) images and electron diffraction (ED) patterns. Advantages of using this technique are: both amplitudes and phases of structure factors are already present in images and very small crystals (<0.5µm) can be used. A preliminary structure model can be deduced from the HREM images by the CRISP crystallographic image processing (CIP) system (Hovmöller S., *Ultramicroscopy* **41** (1992) 121-135).

Usually HREM images have a resolution of less than 2Å, while ED extends beyond 1 Å resolution. A complete 3D ED data can be collected by tilting the crystal. It is generally considered that ED intensities can not be used for structure refinement because of the strong dynamic scattering. However, we have found that for large structures (cell dimensions >10 Å), the ED amplitudes may be close to the X-ray diffraction structure factors (R-value < 25% for Ba<sub>3</sub>Nb<sub>15</sub>O<sub>30</sub>), especially when they are obtained from very thin crystals. The amount of reflections in ED is so large that it should be possible to use them for refining structures to high resolution. Another reason why ED is not very much used for structure determination is the difficulty in obtaining quantitative ED data.

We have developed a program system called ELD for extracting intensities from ED patterns (Zou, X.D., Sukharev, Y. and Hovmöller, S., *Ultramicroscopy* **49**, 1993, in press). The system works on a personal computer. ED patterns are digitized by a CCD camera and transferred to the PC via a frame grabber. ELD, together with CRISP and other programs, aims at making electron crystallography a routine method for structure determination, challenging X-ray crystallography in accuracy, but possible to use for very much smaller crystals.

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An ED pattern of  $\text{Ba}_2\text{Fe}_2\text{O}_5$  as digitized and displayed by ELD. The reflection at the cross is at  $1.45 \text{ \AA}$  resolution.

**PS-02.04.10** A NEW METHOD TO DETERMINE UNKNOWN CRYSTAL STRUCTURE BY ELECTRON DIFFRACTION. BY M. Han\*, Y. X. Cheng, J. Q. Chen, Department of Materials Science and Engineering, Zhejiang University, Hangzhou, 310027, Y. R. Chen, W. X. Liu, Analysis Center, Tianjin University, Tianjin, 300072, P. R. China.

To know the structure of crystal materials is important to investigate the mechanism of various phase transformations. In the general case, however, the determination processes are very difficult for unknown crystals. The principle of a new analysis method which could determine Bravais lattice of unknown crystals by means of three arbitrary and different area-selected electron diffraction patterns is described in this paper. The intersections between two patterns are calculated and verified by computer. Considering two possible relationships, identical axis or different axes, a vector space corresponding a primitive cell of reciprocal lattice is built and reduced. By comparing the reduced result with Niggli reduced cells, the Bravais lattice type and parameters are finally determined. According to these main processes, a computer programme TEM has been already completed by C language. Applying this programme, a successful and convenient method to determine unknown crystal structure is realized. As an example, the structure of mullite has been determined.

## 02.05 – Diffuse Scattering

**MS-02.05.01** MEASUREMENT AND INTERPRETATION OF X-RAY DIFFUSE SCATTERING FROM MACROMOLECULAR CRYSTALS, By D. S. Moss\*, S. A. Butler, Birkbeck College, London, U.K., I. D. Glover, University of Keele, U.K., J. R. Helliwell, University of Manchester, U.K., and M. Adams, University of Oxford, U.K.

Crystals exhibit X-ray diffuse scattering when there is a temporary or permanent breakdown of space group symmetry. Such disorder is particularly prevalent in macromolecular crystals where the Bragg diffraction pattern may only extend to a limited resolution. The advent of area detectors, powerful X-ray sources such as synchrotrons, and high performance computing means that the measurement and interpretation of diffuse scattering from macromolecular crystals is now practicable.

We have modified conventional software for extracting Bragg reflections from scanned X-ray films so that diffuse intensities can be systematically measured.

From the diffuse intensities of 6-phosphogluconate dehydrogenase we have calculated vector correlation maps which show the direction and extent of correlated displacements within the crystals. They show highly anisotropic correlation extending up to about  $30\text{\AA}$ .

We have also interpreted the diffuse scattering in terms of rigid body displacements of domains and secondary structural elements in proteins. We have shown that the diffuse scattering patterns cannot in general be uniquely determined by any one model of rigid body correlation.

Analysis of the components of diffuse scattering has shown that the so-called 'solvent ring' is due mainly to protein diffuse scattering (Acta Cryst. (1991) B47, 960-968). We have also measured the diffuse peaks under the Bragg reflections of ribonuclease-A and have shown that the profile is consistent with the one-phonon approximation.

**MS-02.05.02** COMPUTATION OF DIFFUSE SCATTERING FROM SIMULATED DISORDERED CRYSTALS. By B. D. Butler\*, Research School of Chemistry, Australian National University, Canberra A.C.T. 0200, Australia

A general computer program that can be used to efficiently calculate the diffuse diffraction intensities from large three dimensional (3D) simulated disordered crystals has been developed. The program is suited to crystals that contain both chemical and displacement disorder and was designed to be used with models that have an arbitrary number of distinct atomic species and disordered crystallographic sites per unit cell. The only restrictions on the simulation size are the available computer memory and CPU resources. Diffraction patterns from model systems containing several hundred thousand atoms have been successfully calculated with this program. It has been tested and used on several different computer architectures – ranging from desktop UNIX based workstations to the vector processing (Fujitsu VP2200) and parallel architecture (Thinking Machines CM5) supercomputers – and has been