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

function. In the conventional approach a just significant 3rd order parameter was determined but the existence of fourth order parameters could not be conclusively established because of very high correlation between second and fourth order parameters of the least squares refinement model.
For comparison with results of the conventional treatment, parameters for the anharmonic vibrations have been derived by a 3-dimensional fit of a One Particle Potential model to the MEM nuclear density. Significant values for the cubic term, α_{33}=-0.340(5)eV/Å^3 and a quartic term, β_{20}=9.89(1)eV/Å^4 were found. Maps of the calculated nuclear densities for the assumed model with the above mentioned parameters are shown in Fig.2. In this study it was found that comparison between maps of the MEM nuclear density and maps calculated based on an assumed potential model provided an effective help in determining which model is the most appropriate model for describing the intrinsic anharmonic effects on the nuclear density distribution in Be metal.

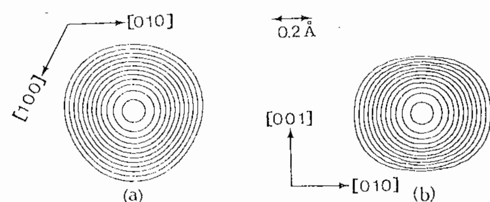

Fig.1 MEM nuclear densities of (a) basal plane and (b)(100).

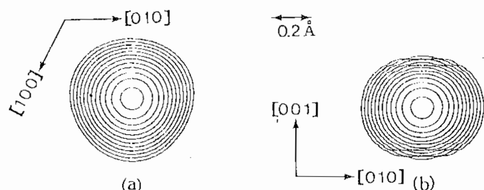

Fig.2 The calculated nuclear density of (a) basal plane and (b) (100).

PS-02.03.10 MAXIMUM ENTROPY METHOD ANALYSIS OF X-RAY AND NEUTRON POWDER DIFFRACTION DATA OF ANATASE.

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In X-ray diffraction, X-ray photons are scattered by electrons in materials, while neutron beams are diffracted by nuclei when there is no magnetic interactions. It is, therefore, appropriated to try to reconstract the electron and nuclear density distribution of the crystalline materials from X-ray and neutron diffraction data, respectively. There have been, however, not known how to restore such electron and/or nuclear density distribution directly from the observed structure factors by diffraction without using any structural model. Recently Sakata & Sato (Acta Cryst., 1990, **A46**, 263-270) has successfully applied the Maximum Entropy Method (MEM) to restore the precise electron density distribution from the accurately determined structure factors. Following to them, it was shown that the accurately measured powder data were suitable for the MEM analysis.

The success of the method depends on the fact that the electron density is always positive. In order to analyse neutron diffraction data by the MEM, it is necessary to overcome the difficulty of negative scattering length for some atoms, such as H, Ti and Mn. In order to overcome the difficulty, Sakata, Uno, Takata & Howard (J. Appl. Cryst., 1993, **26**, in press) has proposed a new method, which deal with, not scattering length densities, but nuclear densities which are always positive. The new method was successfully applied to a rutile (TiO_2) case. This is, however, only one example of the new method. In this paper, the results of MEM analysis for anatase will be given. The data set used in the analysis are collected by powder diffraction experiments for both X-ray and neutron cases.

The MEM maps of anatase are shown in Fig. 1 (a) for electron density and (b) for nuclear density distributions, respectively. In Fig. 1 (a), the chemical bonding state of anatase is very well depicted, which are two kinds of covalant bonding between Ti and O atoms. On the other hand, the nuclear densities in Fig. 1 (b) are simple features of smearing by thermal vibrations. These general features of MEM maps for electron and nuclear densities are very reasonable from physical view point and the present example again proves the usefulness of MEM analysis in crystallography when it is applied to powder diffraction data.

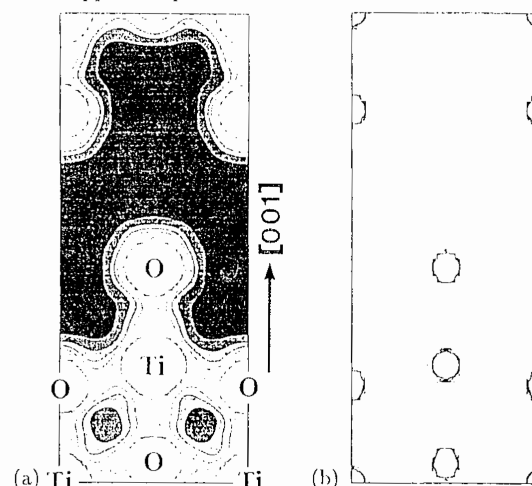

Fig. 1 The MEM maps of anatase (100) plane for (a) electron densities and (b) nuclear densities obtained from powder diffraction data. Contour lines are 0.2 intervals up tp 2.0 e/Å^3 in (a) and 0.1 intervals up to 1.0 x10^{-12} n/Å^3 in (b).

02.04 – Direct Phasing from Electron Diffraction Data for Crystal Structure Analysis

MS-02.04.01 DIRECT PHASING IN ELECTRON CRYSTALLOGRAPHY. By D. L. Dorset* and M. P. McCourt,

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Although the concept of using electron diffraction intensity data for *ab initio* structure analyses was conceived by B. K. Vainshtein, Z. G. Pinsker and their co-workers, acceptance of these data for quantitative determinations is anything but widespread. Recently, the application of traditional direct phasing methods used in X-ray crystallography to electron crystallography, by themselves or in combination with independent phase information from electron microscope images, has shown overwhelmingly that the earlier effort in Moscow was generally correct. Successful analyses have been carried out for small organic compounds, paraffins and their derivatives, linear polymers, larger aromatics with heavier atoms, and even a number of inorganic compounds, either using data collected in the original studies or newer data collected at higher

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

accelerating voltages. Since no information is assumed from any other determination and the results are very close to those found from equivalent X-ray analyses, it must be concluded that quantitative electron crystallography is not the stuff of fantasy and can be equally applied to centrosymmetric and non-centrosymmetric problems. It is even possible to use traditional structure refinement techniques after the initial model is obtained from the first set of phases. This may include Fourier techniques but, if there are enough data, least-squares refinement is also useful. When the only choice for collecting single crystal data is the electron diffraction option with microcrystalline samples, then there is every reason to attempt a structure analysis when intensity data are collected under known constraints to minimize the influence of multiple scattering.
Research supported by NSF CHE91-13899 and NIH GM-46733.

MS-02.04.02 IMAGE DECONVOLUTION AND RESOLUTION ENHANCEMENT IN ELECTRON CRYSTALLOGRAPHY. By F. H. Li, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, P. R. China.

An approach to crystal structure determination combining high resolution electron microscopy and electron diffraction has been established and applied to ordinary crystal structures as well as incommensurate modulated structures. A single high resolution electron microscope image and the corresponding electron diffraction pattern are used throughout the process which consists of two steps: image deconvolution and image resolution enhancement. In the first step, the defocus amount of the image is estimated on the basis of the Sayre equation or the maximum entropy principle. The image is then converted into the structure image with a resolution about 2Å, which is bounded by the resolution of the electron microscope. In the second step, the image resolution is enhanced by a phase extension technique based on the Sayre equation. Amplitudes of structure factors up to 1Å are measured from the electron diffraction pattern. Initial phases within 2Å are obtained by Fourier transforming the structure image resulted from the first step. The resolution of the structure image can be enhanced to about 1Å after the phase extension. The image can be further improved by Fourier recycling.

In dealing with incommensurate modulated structures the initial image is first averaged according to the unit cell of the basic structure and then converted into the average structure image by image deconvolution. Phases of main reflections are obtained from the Fourier transform of the average structure image. The phase extension from main reflections to satellite reflections is carried out based on a multi-dimensional direct method.

MS-02.04.03 FUTURE PROSPECTS FOR DIRECT STRUCTURE RETRIEVAL IN HIGH RESOLUTION ELECTRON MICROSCOPY. D. Van Dyck, University of Antwerp (RUCA), Belgium.

We are living in a very exciting period for structural research using high resolution electron microscopy (HREM). Indeed, the possibility to "see" the individual atoms of which matter is constructed seems within reach. Recent technological improvements allow to obtain a resolution of about 0.1 nm. However, the potential power of the technique is still severely limited by the problem of quantitative interpretation of the images. Thus far the only method to extract structural information from the images consists in comparing the experimental images with computer simulations for various trial structures. For this purpose the Schrödinger equation describing the dynamical electron diffraction as well as the image transfer has to be solved numerically. However this technique is very tedious, requiring a number of usually unknown parameters, and can only be applied with some success if the number of possible structure models is very limited. This makes HREM very much dependent on the availability of prior information obtained from other techniques. HREM would be much more powerful if a direct method exists to extract the structural information directly from the electron micrographs. Recently we proposed a new method to solve this inverse problem. In this method the electron microscope is computer controlled to capture images at very close focus values using a high resolution CCD camera so as to collect all information in 3D image space. By a suitable image processing algorithm it is then possible to retrieve the phase and hence the whole wavefunction in the image plane. From this the influence of the electron microscope aberrations can be eliminated straightforwardly and a projection of the atomic structure of the object can be obtained with a resolution of about 0.1 nm. Recently a Brite-Euram project has been approved for the period 1990-1994 to construct such a microscope. The first prototypes are now in operation and reveal direct 1 Å structural detail. The latest results will be presented and discussed.

MS-02.04.04 DIRECT PHASE DETERMINATION FROM FOURIER TRANSFORMS OF EM IMAGES Sven Hovmöller[1*], Lars Eriksson[1], Xiaodong Zou[1], and Gunnar Svensson[2], Structural[1] and Inorganic[2] Chemistry, Stockholm University, S-106 91 Stockholm, Sweden.

The great advantage of electron microscopy (EM) over X-ray diffraction is that the structure factor phases are not lost. This was shown already in 1968 by DeRosier and Klug (Nature 217, 130-134). Fourier transform (FT) analysis is now a standard technique for EM images of protein crystals.

However, Fourier methods have until now not been much used for studying inorganic crystals by EM. There are two reasons for this, one theoretical and one practical.

From a theoretical point of view there has been doubts about what kind of phase information is available in the EM images and a skepticism about the quality of the amplitudes obtained from EM and electron diffraction. The main practical difficulty has been the lack of an easily available system for crystallographic image processing (CIP). It has been our aim to overcome both these theoretical and practical difficulties.

Images of $Ba_4Nb_{14}O_{23}$ (orthorhombic *Cmmm*, a=20.79, b=12.453, c=4.149 Å) were taken with a Philips CM 30, 300kV electron microscope. Thin areas near the edge were analyzed by our newly developed image processing system, CRISP (Hovmöller, Ultramicroscopy 41 (1992) 121-135). This structure had already been solved by single crystal X-ray diffraction (Svensson and Grins, in manuscript) and refined to an R-value of 3.1%. The amplitudes of the FT of the EM image showed a sharp decrease at 2.4 Å resolution. We interpreted this as being due to the first cross-over of the contrast transfer function of the EM. There were 17 unique reflections inside 2.4 Å resolution, and their phases were determined by CRISP. The phases from EM were compared to the structure factor phases calculated from the highly refined X-ray structure. They were all identical. This shows that the phases obtained in the EM are the same as the X-ray structure factor phases, also for inorganic crystals, provided thin crystals are used.