MS–02.03.06 DIRECT METHODS FOR POWDER DIFFRACTION. By Henk Schenk[*], Jouk Jansen, Pavla Capkova, Wieslav Lasocha, David Rafaja and Rene Peschar, Laboratory for Crystallography, University of Amsterdam, Nieuwe Achtergracht 166, Amsterdam.

The structure determination from powder diffraction data by an 'ab initio' method like Direct Methods is greatly facilitated when as many unique intensities as possible are known accurately. However, powder patterns generally show a range in intensities from 1 to 1000, whereas single–crystal data are found in a much wider range. Then overlap causes complications and, moreover, texture or preferred orientation prevents the intensities to be correct.
Our procedure POWSIM employes for the reconstruction of intensities a two step mechanism. In the first step the complete powder diagram is used in a Rietveld-like procedure applied to the complete diagram (J. Appl. Cryst., 1992, 25, 231), which proves to be an improvement over Pawley's method (J. Appl. Cryst., 1981, 14, 357). By minimizing the least–squares sum of the intensities and background exactly, the fitting becomes independent of the initial intensity and background values. Our results show that the intensities refined with this new technique deviate less from the true intensity values than those from the original Pawley method.
Any curve fitting procedure will never be able to unravel two peaks at the same or nearly the same position. In order to attack this problem, several relations from Direct Methods have been employed to predict which overlapping reflections are strong and which are weak. This information and the sum intensity of overlapping peaks, which is determined correctly by the fitting procedure, can be used to redistribute the intensities in each cluster of overlapping peaks (J. Appl. Cryst.,1992, 25, 231). In this way a vast number of intensities are determined accurately, each of them getting a reliability–index for its accuracy, which is being used in the successive phasing process (Z. Kristall., in the press).
At present fine–tuning of the Direct method is performed and theoretical and practical work is carried out to include texture corrections in the program system. The texture measurements are done with a prototype of a diffractometer, developed in the Philips Research Laboratories (Adv.X–Ray Anal, Vol 31 (1988), Plenum, 413). Also structure determinations using the method will be presented.

PS–02.03.07 ELECTRON DISTRIBUTION IN GERMANIUM BY MAXIMUM ENTROPY METHOD. By H.Ishibashi[*], K.Higashimine, S.Minamigawa and K.Nakahigashi, Department of Materials Science, University of Osaka Prefecture, Japan.

A detailed electron density distribution in germanium was examined from powder X-ray diffraction data. Ultrafine particles of Ge with average particle size less than $1\mu m$ were synthesized by a "hydrogen plasma-metal" reaction method(K. Nakahigashi, H.Ishibashi, S. Minamigawa and M.Kogachi, Jpn. J. Appl. Phys.,1992, 31, 2293-2298). Diffraction intensities were measured by a step scanning with the sampling interval of 0.02° in 2θ and accumulation time was 30 seconds for every step. The scan range in 2θ was from 20° to 145° of $CuK\alpha$ radiation with tube voltage and current of 50kV and 200mA. Integrated intensities were estimated by the computer program WPPD (H.Toraya, J. Appl. Phys.,1986, 440-447). The integrated intensities were converted to the structure factors by the ordinary least-squares refinement. By this analysis, we obtained the values of 11 independent structure factors and one combined structure factor which was a pairs of 333 and 511. The electron density distribution map was drawn by the maximum entropy method (M.Sakata and M.Sato, Acta Cryst.,1990, A42,263-270). A special feature for a diamond structure reappeared well in the map for (110) plane.

However, the bonding electrons were not so clearly observed because of the limited number of reflections measured. In order to improve the map, an experiment using synchrotron radiation is in progress. Results will be presented at the meeting.

PS–02.03.08 CHARGE-DENSITY ANALYSIS BY MEANS OF GAMMA-RAY DIFFRACTION: NiF_2, FeF_2, $SrTiO_3$. By A.Palmer and W.Jauch, Hahn-Meitner-Institut Berlin, Germany.

NiF_2 and FeF_2: Measurements of data sets up to 1.3 $Å^{-1}$ at 295 and 15 K; contrast to MnF_2, combination with neutron diffraction from the identical samples gives no indication for a polarization of the F-atoms in the antiferro-magnetic phase; the population of 3d-orbitals, derived from multipole-models agrees with the expected crystal-field splitting in an octahedral environment.

$SrTiO_3$: Data collection up to 1.6 $Å^{-1}$ at room temperature, at 5 K above the 107 K-structural phase transition and at 50 K; determination of the oxygen position in a single-domain sample; anharmonic thermal motion at RT and asphericities will be reported.

The maximum entropy method (MEM) has been applied to NiF_2 and MnF_2 γ-ray data. It turned out that the failure in mapping the charge-density is not a consequence of insufficient data quality, rather MEM maps are hardly interpretable in the low-density region (Jauch, W. and Palmer, A., Acta Cryst. A, 1993).

PS–02.03.09 DIRECT INVESTIGATION OF ATOMIC THERMAL VIBRATIONS OF BE METAL BY THE MAXIMUM ENTROPY METHOD. By M.Takata[*], M.Sakata, Department of Applied Physics, Nagoya University, Nagoya, 464-01 Japan, S.Kumazawa, Department of Physics, Science University of Tokyo, Noda, Chiba 278 Japan and B.B.Iversen and F.K.Larsen, Department of Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark.

The Maximum Entropy Method(MEM) applied to neutron diffraction data directly yields the nuclear density distribution, which is equivalent to the thermal smearing function. The MEM procedure thus enables us to form maps showing the atomic thermal vibrational features in real space without using a structural model. The purpose of this study is to examine this capability of the MEM for the direct investigation of thermal vibrations and Be was chosen as a test case.
Mean-square atomic displacement and antisymmetric atomic vibrations in Be at room temperature have been determined from short-wave length neutron data by conventional analysis (Larsen,F.K., Lehmann,M.S. and Merisalo,M., 1980, Acta Cryst., A36, 159-163). The same data were treated by the MEM in the present study. The resulting density distribution at the presumed nuclear site in the basal and in the (100) plane of the hcp structure are shown in Fig.1 (a) and (b), respectively. In Fig.1(a) a characteristic triangular feature is clearly visible. We interpret this as being caused by 3rd order anharmonic vibrations in the basal plane. In Fig.1(b) the nuclear density shows significant deviation from the expected oblate shape from harmonic vibrations. We interpret this feature as indicating a significant quartic contribution in the potential

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, $\alpha_{33}=-0.340(5)eV/Å^3$ and a quartic term, $\beta_{20}=9.89(1)eV/Å^4$ 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.
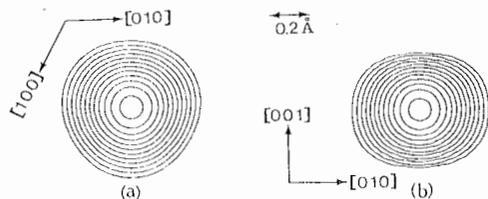

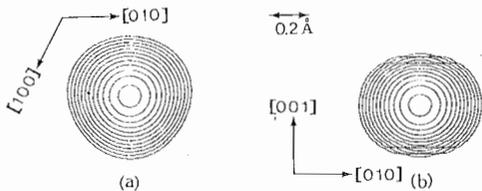**Fig.1** MEM nuclear densities of (a) basal plane and (b)(100).

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.
M. Sakata*, M. Takagi, M. Takata, Department of Applied Physics, Nagoya University, Nagoya, Japan; S. Kumazawa, Department of Physics, Tokyo Science University, Noda, Chiba, Japan; and C. J. Howard, Australian Nuclear Science & Technology Organisation, Lucas Heights, NSW 2234, Australia

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 reconstruct 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 covalent 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.
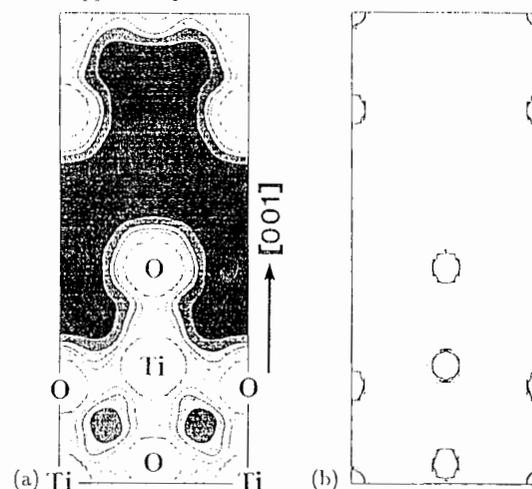

Fig. 1 The MEM maps of anatase (100) plane for (a) electron densities and (b) nuclear densities obtained from powder diffraction data. Contour lines are 0.2 intervals up tp 2.0 $e/Å^3$ in (a) and 0.1 intervals up to 1.0 $x10^{-12}$ $n/Å^3$ in (b).

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, Electron Diffraction Department, Medical Foundation of Buffalo, Inc., 73 High Street, Buffalo, NY 14203 USA

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