

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

MS-02.03.06 DIRECT METHODS FOR POWDER DIFFRACTION.
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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 employs 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. Higashimino, 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 μm 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 $\text{CuK}\alpha$ 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 pair 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 \AA^{-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 antiferromagnetic 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 \AA^{-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