12.4.01 DETERMINATION OF THE SURFACE DEBYE TEMPERATURE IN SEVERAL F.C.C. METALS BY X-RAY DIFFRACTION. By K. Ohshima and J. Harada, Department of Applied Physics, Nagoya University, Nagoya 464, Japan.

The characteristic Debye temperature for fine metal particles $\Theta_p$ decreases with decreasing the particle size due to the increase of the ratio of soft surface phonons to bulk phonons. Such a particle size dependence of $\Theta_p$ permits the determination of the surface Debye temperature $\Theta_s$.

Several F.C.C. metal particles with different mean sizes were prepared by gas evaporation technique (Yatsuya et al., J. Phys. Soc. Jpn. 1973 l2, 1675). The mean sizes were estimated from the widths of X-ray Debye-Scherrer lines with the use of the Hall's relation. The Debye temperatures $\Theta_p$ were determined from the analysis of the temperature dependence of the temperature parameter $B=8\pi^2 u^2$ where $u^2$ is the mean square displacement of atoms. The values of $\Theta_s$ obtained from the particle size dependence of $\Theta_p$ for several F.C.C. metals were summarized in the table together with LEED results. A fairly good agreement between them is noticed, although the surfaces of the present specimens are thought to be not sufficiently clean in comparison with the clean surface in LEED experiments.

<table>
<thead>
<tr>
<th>$\Theta_s$ (X-ray)</th>
<th>$\Theta_s$ (LEED)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au 96(6)</td>
<td>80(10)K</td>
</tr>
<tr>
<td>Ag 135(10)</td>
<td>128(10)</td>
</tr>
<tr>
<td>Cu 182(20)</td>
<td>205</td>
</tr>
<tr>
<td>Pb 65(5)</td>
<td>55(10)</td>
</tr>
</tbody>
</table>

12.5.01 PRECISION PROFILE FITTING X-RAY POWDER DATA FOR CRISTAL STRUCTURE REFINEMENT. By Ch. Parrish and T. C. Huang, IBM Research Laboratory, San Jose, Ca. 95193, USA.

The refinement of crystal structures using precision X-ray powder diffractometer data and our profile fitting method (PPM) has given good results. The PPM accurately determines the integrated intensities and reflection angles (Parrish & Huang, Nat. Bur. Stand. Spec. Pub. 567, P. 95, 1980). The wavelength distribution $\lambda$ and the geometrical aberrations $G$ define the instrument function $W_0^G$ which is accurately represented in PPM by a sum of Lorentzian curves. The true diffraction from the specimen $S$ can therefore be precisely determined from the convolution $W_0^G S$. The integrated intensity, 28 and line width of each reflection together with the linear background are determined from the best match of calculated and experimental patterns. Because the shapes of $W_0^G$ and $S$ have been established for all scattering angles and the profile parameters and background are simultaneously determined, a close match is obtained with $R$ typically about 3% and $R_I$ about 0.5%.

The PPM resolves overlaps without prior data on the number of reflections or their angles. For very close overlaps or clusters the known reflections and their 28s (derived from atomic parameters) may be entered to increase the resolution in determining the intensities.

12.5.02 A PATTERN-FITTING STRUCTURE-REFINEMENT PROGRAM FOR X-RAY POWDER DATA. By Ch. Baerlocher and A. Hepp, Institute of Crystallography and Petrography, ETH, 8092 Zurich, Switzerland.

A program package, designed specifically for X-ray powder diffraction data and capable of refining structures with more than 100 structural parameters, has been developed for the profile-fitting method. It is based on the X-ray System (J.M. Stewart et al. University of Maryland) and utilizes all its advantages (e.g. binary data file, variable memory allocation etc).

First, a standard peak-shape function is determined in tabulated form from the observed profile by a new algorithm. The procedure is not based on an analytical function and therefore any experimental peak shape can be fitted accurately. The 28-dependence of the peak width and the asymmetry is also evaluated from the profile in numerical form.

In order to supplement the diffraction data, known interatomic distances and angles can be included as weighted constraints and/or their expected ranges be imposed as boundary conditions. These additional observations stabilize the least-squares convergence and are essential in the refinement of larger problems.

The program system offers a choice of two different LS procedures, the Newton-Gauss or matrix inversion or a variable metric algorithm (W.C. Davidson, Mathematical...
Programming (1975), 9, 1-30. The latter is less sensitive with respect to high correlation since it uses a positive definite matrix with elements converging towards the second order derivatives of the function. This greatly improves the behavior around ill-defined minima, which are frequently encountered in the Rietveld method (R.A. Young (1980), NBS Special Publication 567, 143-162).

In addition to structural parameters, the program can refine lattice constants, a linear 2θ correction, peak half width and asymmetry, and preferred orientation. It can also handle the broadening of individual lines due to crystallite shape or lattice strain. The data input is kept to a minimum and is partly in free format. At the moment the program requires strictly monochromatic diffractometer data, which are necessary to achieve good resolution. Neutron data can also be employed.

The programs have been successfully tested in a number of different structure refinements including that of zeolite ZSM-5. This zeolite has an orthorhombic structure with a cell of 20x20x13 Å³ and 134 positional parameters. The X-ray data were supplemented with 165 distance and angle constraints.

12.5.03 ANALYSIS OF TIME-OF-FLIGHT DATA FROM A RESOLUTION FOCUSED NEUTRON POWDER DIFFRACTOMETER. By R.B. Von Dreele, Department of Chem., Artz. State Univ., Tempe; H. Soper, Los Alamos Scientific Laboratory, Los Alamos, N.M.

The resolution focused powder diffractometer at the WNR neutron pulsed source has five counter banks positioned at average 2θ values of 150, 90, 40, 12.5 and 7° having 16, 16, 16, 6 and 3 detectors each, respectively. The banks are tilted so that all tubes in a bank have the same resolution (2θ/d) for a given d-spacing. Because the resolution focusing condition is not the same as the time focusing condition for a given counter bank, the spectra associated with the counters in a bank do not coincide in time and must be recorded separately.

The methods used to reduce the 62 individual spectra to a more manageable number and some results from Rietveld refinement of the merged data from some test samples will be presented.

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12.5.04 USE OF THE COMPUTER CONTROLLED POWDER DIFFRACTOMETER FOR THE CRYSTAL STRUCTURE DETERMINATION OF SEVERAL RARE EARTH MAGNESIUM FLUORIDES. By R. Jenkins, and R. Banks, Polytechnic Institute of New York, Brooklyn, NY.

This paper describes the use of the computer controlled powder diffractometer for the determination of the crystal structures from powder data, using as examples of several Rare Earth Magnesium Fluorides. The lack of specimens of sufficient purity precluded use of profile fitting techniques so use was made of more classical methods of peak location and intensity measurement. An attempt was made to establish the limitations of such a procedure both in the accuracy obtainable in terms of cell parameters and also in the calculation of atomic arrangement.

Three materials were examined, these being the mixed Magnesium Fluorides of Eu, Sm and Sr. Orthorhombic structures were assigned and the unit-cell dimensions were found to be 
- for SmF₃: 3.95, 14.43 and 5.66Å; for
- for SrF₃: 3.917, 14.51 and 5.67Å.

It was estimated that the accuracy of the cell parameter data is of the order of 3 parts per 10,000. Each unit cell had 24 atoms corresponding to 4 formula weights/cell. R-factors of 0.10, 0.17 and 0.18 were found for the three structures respectively.

Rare Earth and Strontium atom was found to be in 8-fold coordination with the Fluorine atoms and the Magnesium atom in 6-fold coordination with the Fluorines. The Rare Earth and Strontium atom to Fluorine distance was found to be 3.32-2.68Å and the average Magnesium to Fluorine distance 2.03Å. These distances are in agreement with the values of 2.55Å and 2.03Å reported by Shannon.

12.5.05 X-RAY GUINIER POWDER PROFILE REFINEMENT OF Rb₂NaHoF₆ AT 17 K. By J. Ihringer, Inst. f. Kristallographie der Universität Tübingen, D-7400 Tübingen, West Germany; E.J. Veenendaal, Kammerlingh Onnes Laboratorium der Rijksuniversiteit te Leiden, Netherlands

Rb₂NaHoF₆ (Pm3m, a = 8.6622(2) Å at 205 K) exhibits a T' point phase transition at 17 K with a continuously increasing tetragonal distortion. The diffraction pattern (59 <θ< 46.2°) at 17 K was recorded with an automated low temperature Guinier diffractometer (Ihringer, J. of Appl. Cryst. (1980) in press). For the structure refinement the modified Rietveld program (Young, Mackie & von Dreele, J. Appl. Cryst. (1977) 10 262) with correction factors appropriate to the Guinier geometry was used.

All models resulting from a one phonon T-point condensation were considered. The best final residual of 4.6% was found for the space group 14/m (T=17 K, a=6.2233(2), c=8.8975(3) Å, V=344.53 Å³). The NaF₆ octahedra remain undistorted, but they are tilted around the (001) axes within an angle of 5.45 deg. This kind of distortion is well known from the phase transitions in perovskites or K₂PbCl₄ structures. In Rb₂NaHoF₆, however, the tetragonal distortion - a tetragonal distortion - is being developed without any measurable discontinuity (Δa,Δc<0.007 Å), and increases almost linearly with decreasing temperatures. The mechanism of the lattice stability below the phase transition will be discussed.