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,
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sity, Nagoya 464, Japan

The characteristic Debye temperature for fine
metal particles Θ_p decreases with decreasing
the particle size due to the increase of   ra-
tio of soft surface phonons to bulk phonons.
Such a particle size dependence of Θ_p permits
the determination of the surface Debye tempera-
ture Θ_s.
    Several F.C.C. fine metal particles with
different mean sizes were prepared by gas evap-
oration technique(Yatsuya et al.,J.Phys.Soc.
Jpn.(1973)12,1675). The mean sizes were esti-
mated from the widths of X-ray Debye-Scherrer
lines with the use of the Hall's relation. The
Debye temperatures Θ_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 Θ_s obtained from the particle size
dependence of Θ_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 pre-
sent specimens are thought to be not suffi-
ciently clean in comparison with the clean sur-
face in LEED   experiments.

	Θ_s (X-ray)	Θ_s (LEED)
Au	96(6) K	80(10)K
Ag	135(10)	128(20)
Cu	182(20)	205
Pb	65(5)	55(10)

12.5-01   PRECISION PROFILE FITTING X-RAY POWDER DATA
FOR CRYSTAL STRUCTURE REFINEMENT.   By W. Parrish and
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The refinement of crystal structures using precision
X-ray powder diffractometer data and our profile fitting
method (PFM) has given good results. The PFM accurately
determines the integrated intensities and reflection
angles (Parrish & Huang, Nat. Bur. Stand. Spec. Pub. 567,
P.95, 1980). The wavelength distribution W and the
geometrical aberrations G define the instrument function
W*G which is accurately represented in PFM by a sum of
Lorentzian curves.   The true diffraction from the
specimen S can therefore be precisely determined from
the convolution (W*G)*S. The integrated intensity, 2θ
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*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 RI about 0.5%.

The PFM resolves overlaps without prior data on the
number of reflections or their angles. For very close
overlaps or clusters the known reflections and their 2θs
(derived from lattice parameters) may be entered to
increase the resolution in determining the intensities.

The collection of accurate powder data requires extreme
care in specimen preparation and experimental techniques.
Rotating flat samples of 5-10 and 10-20 μm powders were
used. The diffractometers were automated with an IBM
Series/1 minicomputer using step scanning with Δ2θ and t
determined from preliminary scans. For the final data we
sometimes used overnight runs to pick up weak peaks,
resolve difficult overlaps and obtain high statistical
accuracy. The diffractometer was equipped with vacuum
path, diffracted beam focussing graphite monochromator

and scintillation counter with pulse amplitude discrimi-
nation. All experimental data were corrected for the
resolving time of the detector and circuits.

The methods were tested with Si, Al_2O_3, SiO_2 and
Mg_2SiO_4. The structure refinements gave R-values of 1-3%.
The full powder patterns calculated from the refinement
results very closely matched the experimental patterns
with Rs and RIs as low as those obtained by PFM. The
figure below is a typical pattern of quartz. The curve
is the pattern calculated from the structure refinement
results, and the differences between calculated and
observed data are shown on the top. This research was
done in collaboration with G. Will who carried out the
POWLS refinements.

R = 2.3%
RI = 0.1%
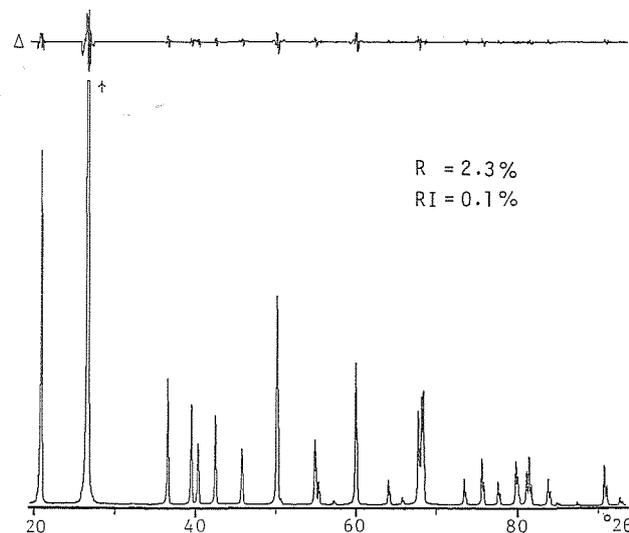
12.5-02   A PATTERN-FITTING STRUCTURE-REFINE-
MENT PROGRAM FOR X-RAY POWDER DATA. By Ch.
Baerlocher and A. Hepp, Institute of Crystal-
lography and Petrography, ETH, 8092 Zurich,
Switzerland.

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 there-
fore any experimental peak shape can be fitted
accurately. The 2θ-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
matrix inversion or a variable metric
algorithm (W.C. Davidon, 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 A^3 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., Ariz. State Univ., Tempe, Ariz. 85281 and A. 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 8 detectors each, respectively. The banks are tilted so that all tubes in a bank have the same resolution ($\Delta d/d$) 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.

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 E. 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 elucidation 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 $EuMgF_4$: 3.395, 14.43 and 5.664Å; for $SmMgF_4$: 3.695, 14.44 and 5.661Å and for $SrMgF_4$: 3.917, 14.51 and 5.637Å. It is 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. Each Rare Earth and Strontium atom was found to be in 8-fold coordination with the Fluorine atoms and the Magnesium atoms in 6-fold coordination with the Fluorines. The Rare Earth and Strontium atom to 6-fold coordination with the Fluorines. The Rare Earth and Strontium atom to Fluorine distance was found to be 2.32-2.8Å and the average Magnesium to Fluorine distance 2.03Å. These distances are in agreement with the values of 2.55Å and 2.02Å reported by Shannon.

12.5-05   X-RAY GUINIER POWDER PROFILE REFINEMENT OF Rb_2NaHoF_6 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

Rb_2NaHoF_6 (Fm3m, a = 8.8622(2) Å at 205 K) exhibits a Γ-point phase transition at 170 ± 5 K with a continuously increasing tetragonal distortion.
The diffraction pattern (5° $<\theta<$ 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 Γ-point condensation were considered. The best final residual of 4.6 % was found for the space group I4/m (T=17 K, a=6.2233(2), c=8.8957(3) Å V=344.53 $Å^3$). The NaF_6 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 K_2PtCl_6 structures. In Rb_2NaHoF_6, however, the tetragonal distortion $-$ a sterical result of the tilted octahedra $-$ is being developed without any measurable discontinuity ($\Delta a, c \leq 0.007$ Å), and increases almost linearly with decreasing temperatures. The mechanisme of the lattice stability below the phase transition will be discussed.