

**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 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. fine metal particles with different mean sizes were prepared by gas evaporation technique (Yatsuya et al., J. Phys. Soc. Jpn. (1973) 12, 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  $B=8\pi^2\langle u^2 \rangle$  where  $\langle u^2 \rangle$  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.

	$\Theta_s$ (X-ray)	$\Theta_s$ (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 T. C. Huang, IBM Research Laboratory, San Jose, CA. 95193, USA.

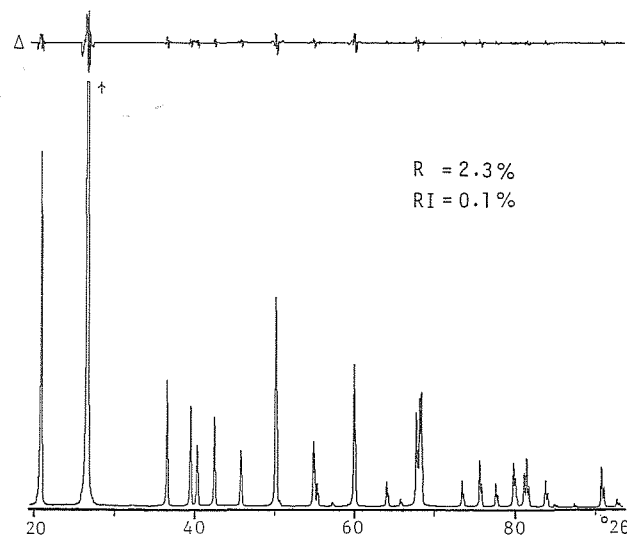
The refinement of crystal structures using precision X-ray powder diffractometer data and our profile fitting method (PFM) has given good results. The PFM accurately determines the integrated intensities and reflection angles (Parrish & Huang, Nat. Bur. Stand. Spec. Pub. 567, P.95, 1980). The wavelength 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,  $2\theta$  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  $2\theta$ s (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  $\mu\text{m}$  powders were used. The diffractometers were automated with an IBM Series/1 minicomputer using step scanning with  $\Delta 2\theta$  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 discrimination. All experimental data were corrected for the resolving time of the detector and circuits.

The methods were tested with Si,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and  $\text{Mg}_2\text{SiO}_4$ . 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  $R_s$  and  $RI_s$  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.



**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  $2\theta$ -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