s8.m27.o3 **Anisotropic Microstrain-Like Diffraction-Line Broadening Due to Composition Variations and Other Origins.** Andreas Leineweber and Eric Jan Mittemeijer, *Max Planck Institute for Metals Research, Germany. E-mail: a.leineweber@mf.mpg.de*

Keywords: Powder Diffraction; Line-Profile Analysis; Rietveld Refinement

In the course of fitting procedures considering complete powder diffraction profiles (e.g. Rietveld refinement) often the problem arises to describe anisotropic diffraction-line broadening appropriately. Sometimes, purely empirical approaches are adopted, e.g. if the line-profile is not of interest itself. But more frequently 'size' and 'microstrain' broadening contributions and their anisotropies are dealt with separately. Often it is desired to extract the physical information supplied by the anisotropic line-broadening. For that purpose it is necessary to incorporate into the fit routines the anisotropies of 'size' and 'microstrain' broadening in a way compatible with their physical origins. In many cases of anisotropic microstrain broadening the width of a reflection on the 2θ scale varies for a certain direction of the diffraction vector with $\tan\theta_{hkl}$:

$$B_{hkl} = A(hkl) \times \tan\theta_{hkl} \qquad (1)$$

where B_{hkl} quantifies the width of the reflection hkl (e.g. the full width at half maximum) and $A(hkl)$ is an anisotropy factor, which varies with the direction of the diffraction vector, but not with θ_{hkl}. Assuming no specific physical origin for the microstrains and their probability density function a phenomeno¬logical expression for the anisotropy factor was derived on the basis of statistical considerations [1,2]:

$$A(hkl) = d_{hkl}^2 \times \sqrt{\sum_{H+K+L=4} S_{HKL} h^H k^K l^L} \qquad (2)$$

where d_{hkl} corresponds to the average d-spacing of the reflection hkl, and S_{HKL} are fit parameters with restrictions imposed due to crystal symmetry, and H,K,L are exponents for h,k,l. It can be shown that certain physical origins of microstrain which are caused by local variations of a single scalar variable ξ (e.g. composition, temperature ...) [3] lead to an anisotropy factor of

$$A(hkl) = d_{hkl}^2 \times \left| \sum_{H+K+L=2} D_{HKL} h^H k^K l^L \right| \qquad (3)$$

with fitting parameters D_{HKL} which have again restrictions imposed due to crystal symmetry, and which are related to the width of the distribution of ξ and the derivatives of the components of the reciprocal metrical tensor with respect to ξ. Eq. (3) constitutes a special case of Eq. (2), and thus the physical origins of line broadening leading to Eq. (3) can also be fitted using Eq. (2), however with redundant fitting parameters. Practical examples for both symmetric and asymmetric anisotropic diffraction-line broadening according to Eq. (3) will be presented (in particular due to composition variations), as well as model cases for which specific physical origins of microstrain line-broadening lead to anisotropies compatible with Eq. (2) and/or (3). Furthermore, possible advantageous alternative formulations of Eqs. (2-3) will be discussed.

[1] Popa, N.C., *J. Appl. Crystallogr.* **31** (1998) 176.
[2] Stephens, P.W., *J. Appl. Crystallogr.* **32** (1999) 281.
[3] Leineweber, A. & Mittemeijer, E.J., *J. Appl. Crystallogr.* **37** (2004) 123.

s8.m27.o4 **Joint-Probability Methods for Indexing Impure and Multi-Component Powder Diffraction Patterns**. Robin Shirley, *School of Human Sciences, University of Surrey, Guildford, Surrey GU2 7XH, U.K. E-mail: R.Shirley@surrey.ac.uk*

Keywords: Powder; Indexing; Joint-probability

In general, a polycrystalline material will give a diffraction pattern in which the well-resolved three-dimensional reciprocal lattice of its single crystal has been collapsed by rotational averaging into the much less well-resolved one-dimensional sequence of diffraction peaks that make up its powder diffraction pattern. In the resulting profile, all explicit three-dimensional information has been lost, leaving only the convolution of observational functions with a set of radial distances d* in reciprocal space (the inverse of the corresponding interplanar distances d).

Even if recorded at high resolution at a synchrotron source or with a modern focusing laboratory diffractometer, as a powder profile moves into regions of higher d* (or the equivalent in diffraction angle 2Theta) it will increasingly become degraded by line overlap and by incompleteness through loss of intensity. Calculated powder peaks change position so readily with small changes in lattice constants that in practice those higher-angle lines which it is possible to measure reliably place relatively few constraints on proposed cells.

In many real-world cases, such as pharmaceutical drug-discovery materials or the products of high-temperature, high-pressure experiments, diffraction features from additional solid phases will also be present, such as polymorphs, reaction by-products, or unidentified impurities.

Before the unknown structure(s) of the major phase(s) can be determined, their three-dimensional reciprocal lattice(s) must be reconstructed from the information implied in the observed one-dimensional profile, in the face of these difficulties. This is not easy. Although of course the underlying physical problem has a definite and unique solution, that is not guaranteed to be true of the much less well-determined problem of cell recovery from powder data.

This paper will report current progress on computer-based methods for lattice reconstruction (powder indexing) using joint-probability-based quality measures such as Ir and Pr. These have the valuable property of reporting the amount of fit (rather than misfit) to the observed diffraction data given by partial lattice models, in the presence of arbitrary non-model features such as any undetermined lattice constants, diffraction from additional solid phases, impurity lines and other artifacts.

It will be shown that, given well-measured data, it is possible to reconstruct unit cells correctly from the diffraction patterns of impure low-symmetry samples that contain 10 or more impurity lines, and in favourable (i.e. non-pathological) cases to recover the unit cells from each of the components of multiphase samples containing two or more unknown low-symmetry solid phases. Programs to be discussed include Hmap and Peurist, within the latest 32-bit version of the Crysfire powder-indexing expert system [1, 2].

[1] R. Shirley (2004), *The Crysfire 2004 System for Automatic Powder Indexing: User's Manual*, Lattice Press: Guildford, U.K.
[2] http://www.ccp14.ac.uk/tutorial/crys/