

PREFACE

Microstructure Analysis by Diffraction— The Beginning of the End



The phenomenon of X-ray diffraction by a crystalline material is most fundamentally based on the scattering of X-rays by the periodically repeating array of atoms which compose the unit cell. Thus, the primary features of a powder pattern, the location and intensity of the diffraction maxima, give information about the periodic atomic structure of the material. The location of diffraction peaks depends only on the size and shape of the unit cell and the wavelength of the X-rays used. The square of the reciprocal of the interplanar spacing, d_{hkl}^{*2} , is related to the lattice parameters by the well known d^{*2} equation,

$$d_{hkl}^{*2} = h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2} + 2hka^* b^* \cos \gamma^* + 2hla^* c^* \cos \beta^* + 2klb^* c^* \cos \alpha^*. \quad (1)$$

The interplanar spacing d_{hkl} obtained from Eq. (1) goes into Bragg's law

$$N\lambda = 2d_{hkl} \sin \theta, \quad (2)$$

along with the wavelength, to predict the angle at which this diffraction line could appear. The other primary feature of a diffraction line is its intensity which depends only on the experimental conditions and the crystal structure according to Eq. (3).

$$I_{(hkl)} = \left[\frac{I_0 \lambda^3}{64\pi r} \left(\frac{e^2}{m_e c^2} \right) \frac{M_{hkl}}{V^2} |F_{(hkl)}|^2 \left(\frac{1 + \cos^2 2\theta \cos^2 2\theta_m}{\sin^2 \theta \cos \theta} \right)_{hkl} \mu^{-1} \right]^2. \quad (3)$$

The principal applications of powder diffraction during the 20th century have been qualitative, quantitative and crystal structural analysis. Each of these tools depends solely on the primary features of the powder diffraction pattern-determined by the crystal structure. The advent of computer automated diffractometers has permitted routine determination of powder diffraction patterns to degrees of precision rarely ever attained previously. Thus, beginning in the 1980's, the techniques for carefully analyzing diffraction maxima shapes and studying the secondary pattern features began to blossom. In general, the deviations of a particular specimen, from the ideal or perfect periodic crystal structure, cause diffraction peak profiles to broaden and sometimes to become asymmetric. Thus, information on the *real* structure or *microstructure* of a specimen can be obtained from a careful study of the diffraction line profiles.

Scherrer, in the earliest days of diffraction analysis, recognized that crystallite size will broaden diffraction lines according to Eq. (4) which relates β , the integral breadth of a peak (similar to the Full Width at Half Maximum), to the average crystallite size D .

$$\beta = \frac{k\lambda}{D \cos \theta}. \quad (4)$$

Micro-strain (ϵ or $\frac{\Delta d}{d}$), which causes d value variations around an average, also causes peak broadening according to

$$\beta = 4 \frac{\Delta d}{d} \tan \theta. \quad (5)$$

The difference in the functional dependence of these two effects on theta led Warren and Averbach in the 1930's to develop their classical Fourier technique for separating them. The advent of fast inexpensive computers has more recently led to direct deconvolution of the specimen contribution to broadening and Williamson-Hall size-strain analysis in experiment (θ) space rather than Fourier space.

Other techniques for microstructure analysis from diffraction patterns such as macro-strain and preferred orientation analysis have evolved well over the years however, the effects of crystallographic *mistakes* on peak asymmetry and the effect of the *distribution* of small crystallites on the tails of diffraction peaks is not well understood.

It seems to me that as we approach a new century we are on the threshold of a new approach to powder diffraction analysis in which the whole pattern will be used to constrain and guide algorithms which will fully model both the primary crystal structure based aspects and the secondary, microstructure dependent, effects on a powder pattern. The 20th century has brought the primary analysis to a state of substantial sophistication however, only the most dramatic effects of microstructure are modelable today. The path toward a total fit of the full experimental pattern including the types and densities of stacking faults, an understanding of the strain field produced by each and its effect on diffraction profiles now appears to me to be a realizable goal. This task will not complete soon or simply but the sign posts are now in place pointing the way to what I believe will produce a complete microstructural analysis of materials by whole pattern modeling. There is a chance that the complete understanding and computation of the powder diffraction pattern may be achieved by 2015, the 100 year anniversary of the recording of the first powder patterns by Debye, Scherrer and Hall.



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