

A New Perspective on X-Ray Scattering for More Accurate Powder Diffraction Analysis

Dr. Anil Kumar

Associate Professor of Chemistry, GGM Science College Jammu, India

Email: [aneilverma\[at\]gmail.com](mailto:aneilverma[at]gmail.com)

Abstract: *This article proposes a new theory of X-ray scattering that has particular relevance to powder diffraction. The underlying concept of this theory is that the scattering from a crystal or crystallite is distributed throughout space: this leads to the effect that enhanced scatter can be observed at the 'Bragg position' even if the 'Bragg condition' is not satisfied. The scatter from a single crystal or crystallite, in any fixed orientation, has the fascinating property of contributing simultaneously to many 'Bragg positions'. It also explains why diffraction peaks are obtained from samples with very few crystallites, which cannot be explained with the conventional theory. The intensity ratios for an Si powder sample are predicted with greater accuracy and the temperature factors are more realistic. Another consequence is that this new theory predicts a reliability in the intensity measurements which agrees much more closely with experimental observations compared to conventional theory that is based on 'Bragg-type' scatter. The role of dynamical effects (extinction etc.) is discussed and how they are suppressed with diffuse scattering. An alternative explanation for the Lorentz factor is presented that is more general and based on the capture volume in diffraction space. This theory, when applied to the scattering from powders, will evaluate the full scattering profile, including peak widths and the 'background'. The theory should provide an increased understanding of the reliability of powder diffraction measurements, and may also have wider implications for the analysis of powder diffraction data, by increasing the accuracy of intensities predicted from structural models.*

Keywords: diffraction theory; powder diffraction; small crystals

1. Introduction

The concept of Bragg's law assumes that the scattering is concentrated at discrete points and that away from these positions the mutual interference gives no significant scattering (Bragg, 1925). An alternative viewpoint is presented here, where the whole of diffraction space is occupied by scattering from many crystal planes, which when combined contribute to the peaks observed. This effect is most obvious in X-ray powder diffraction and this is therefore the main focus of this article. X-ray powder diffraction was pioneered by Debye & Scherrer (1916) and is now a well established technique that has been used successfully for nearly 100 years. This is a very important technique for the identification of material phases and their quantitative proportion, microstructure evaluation and molecular structure determination. A powder is in general an accumulation of small crystallites with dimensions 10 nm or less. Most materials have some identifiable atomic periodicity and therefore create an X-ray diffraction pattern. This gives X-ray powder diffraction an important role in many industries from building materials, pharmaceuticals, mining, forensic analysis etc., to scientific studies on the evaluation of the microstructure and the determination of the stereochemistry of molecular structures. These analyses give information on the strength of materials, liability to cracking in structures, identification of polymorphs in drug design, identification of phases and their proportions in paints and cement etc. Its impact worldwide has been enormous and many important processes depend on X-ray powder diffraction. However, the 'standard explanation' of the diffraction process raises some concerns: for example, the low probability of Bragg scattering (Fewster, 2000), the high variability in peak shapes depending on experimental procedure (Fewster & Andrew, 1999) and the poor reliability of intensity measurement based on crystal statistics (Smith, 1999). Despite these concerns, the method seems to work. It

is the position, width and intensity of the diffraction peaks that yield the information for the analyses mentioned above. This article will give a brief outline of the conventional theory of X-ray powder diffraction and its shortcomings, including the theoretical estimates of crystal statistics and estimates of temperature factors, followed by an alternative theory that addresses these weaknesses. Attention will be drawn to the relevance of dynamical and kinematical scattering and the origin of the intensity, the improvement in the intensity estimates when compared with measured values and the complex nature of the intensity distribution. The whole process, based on this alternative theory, is much more subtle and fascinating than can be explained by the simple application of Bragg's law. This improved understanding has led to, and may in the future lead to further, new diffractometer designs, more robust analyses of the data and a firmer basis for establishing the reliability of the method.

Geometrical Interpretation and the General Case

A consideration of the geometry of the shape transform shown in Fig. 6 enables us to see why we observe a specular peak in intensity for this particular cubic shaped crystal, why this crystal also provides a peak in scattered intensity at an angle close to (but not exactly at) the Bragg angle when it is oriented from the Bragg condition, and why in the general case NTKRD is incorrect. The specular peak can be explained as follows. For an orthorhombic shaped crystal, with the facets cut as described thus far, the sinc functions associated with the shape transform form 'arms' of intensity parallel to the k_x ; k_y ; k_z axes in reciprocal space. If the reflection in which we are interested has a reciprocal-lattice vector which lies along one of these arms then the arms of the shape function form a chord on the Ewald sphere (for the crystal cut as described here, any reciprocal lattice vector in the family $\{m00\}$ will meet this criterion). As can be seen from Fig. 6 the length of this chord will change as we vary,

but at a scattering angle 2θ such that the reflection is always specular – a point to which we will return later. The constructions in reciprocal space also allow us to see why we obtain some, albeit weak, scattering at close to (but not exactly at) the Bragg angle as this particular crystal is rotated for scattering associated with this particular reciprocal-lattice vector. Consider Fig. 7(a), where we show the shape transform for our cubic crystal at the Bragg condition and slightly rotated away from it. As an arm of the shape transform at the Bragg condition is perpendicular to the reciprocal-lattice vector, the position where the Ewald sphere crosses the arm of the shape transform is such that the angle of 2θ at such a point is initially a slowly varying function of the angle of rotation.

2. Conclusion

The effects that the finite size of crystals has on X-ray diffraction have been discussed and considered since soon after the foundation of the field. Within NTXRD mistakes are made in summing the phases of scattered X-rays from a crystal with an orthorhombic shape, which lead to the incorrect conclusion that such crystals always have some peak in scattering at the Bragg condition. It is also claimed that this result holds for crystals of a general shape. As we have shown, these conclusions are in error, and the effects that the shape and finite size of crystals have on the diffraction pattern are well described by conventional diffraction theory. Whilst a study of finite crystallite size effects will no doubt continue to be of importance in relating experimental and computed diffraction profiles, and the experimental data presented in Fewster (2014) and Fewster (2016) are no doubt worthy of further study, the specific claim made within NTXRD that simple theory predicts a peak in the scattered intensity to occur exactly at the Bragg condition when small crystallites are rotated away from that condition is false. Acknowledgements The authors would like to thank Professor A. M. Glazer for bringing the work within NTXRD to their attention and for useful discussions. We are also grateful to a particularly assiduous anonymous referee of this manuscript who went to the considerable trouble confirm our results by reproducing our within their report by use of both an analytic approach and brute force atomistic simulations.

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