# Polarization Effects of X-ray Monochromators Modeled Using Dynamical Scattering Theory

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#### Abstract

The difference in the diffracted intensity of the  $\sigma$  and  $\pi$  polarized components of an X-ray beam in powder diffraction has generally been treated according to equations based on dipole scattering, also known as kinematic X-ray scattering. Although this treatment is correct for powders and post-sample analyzers known to be of high mosaicity, it does not apply to systems configured with nearly-perfect-crystal incident beam monochromators. We present equations for the polarization effect, based on dynamical diffraction theory applied to the monochromator crystal. The intensity of the  $\pi$  component relative to the  $\sigma$  component then becomes approximately proportional to  $|\cos 2\theta_{\rm m}|$ rather than to  $\cos^2 2\theta_{\rm m}$ , where  $\theta_{\rm m}$  is the Bragg diffraction angle of the monochromator crystal. This changes the predicted intensities of X-ray powder diffraction patterns produced on instruments with incident beam monochromators, especially in the regions far from  $2\theta = 90^{\circ}$  in the powder pattern. We present experimental data, based on well-known Standard Reference Materials, confirming that the dynamical polarization correction is required when a Ge 111 incident beam monochromator is used. The dynamical correction is absent as an option in most modern Rietveld powder diffraction analysis codes.

#### 1 Introduction

The relative intensity of diffraction peaks is an important measurand in a variety of powder diffraction experiments. A correction for the effects of polarization on intensity as a function of diffraction angle is a ubiquitous feature of any Rietveld analysis code. The unpolarized X-ray radiation can be considered as two components, the  $\sigma$ -polarized radiation with the electric field perpendicular to the diffraction plane, and the  $\pi$ -polarized component with the electric field in the diffraction plane. To accurately model the intensity over the full range of diffraction peaks requires that the difference in the diffracted intensity of the  $\sigma$ -polarized X-ray radiation and the  $\pi$ -polarized component, be considered as function of  $2\theta$  angle. In a typical laboratory system, the incident beam is produced by an X-ray tube with an electron beam impinging on a metal anode, and the emitted X-rays are considered to have identical intensity for the  $\sigma$  and  $\pi$ components (*i.e.* unpolarized). However, if the beam is diffracted from a crystal, the relative intensity of the two components is modified.

The independent-dipole scattering approach is essentially equivalent to the kinematic theory of X-ray scattering, and is appropriate for materials in which the loss due to absorption exceeds the strength of the reflected beam. This is certainly true for materials such as finely powdered specimens, and Highly Oriented Pyrolytic Graphite (HOPG) crystals commonly used as post-sample analyzers. These are prepared to be of high mosaicity so as to offer an energy bandpass of sufficient breadth that the emission spectrum of the incident beam is fully transmitted. Since much of powder diffraction has historically been carried out using either an unpolarized beam scattered directly into a detector, or via a post-sample analyzer consisting of a HOPG crystal in front of the detector, the kinematic treatment has been appropriate. However, the powder diffraction community as a whole has been content to also apply this approach to polarization effects due to single crystal optics, which do not act as independent dipole scatterers.

Historically, this correction has followed the work of Blake [1933] where a correction based strictly on the dipole scattering from individual atoms is made. In the dipole scattering approximation, if the incoming electric field vector  $\vec{E}_i$  is perpendicular to the plane containing the incoming and outgoing rays ( $\sigma$  polarization), the intensity of scattering is independent of the azimuthal angle around  $\vec{E}$  (which is the diffraction angle  $2\theta$ ), since  $\vec{E_i}$  is parallel to the outgoing  $\vec{E_{o}}$ . On the other hand, for scattering with  $\vec{E_{i}}$  lying in the plane containing the incoming and outgoing rays  $(\pi \text{ polarization}), \vec{E_o}$  is at a polar angle  $2\theta$  to  $\vec{E_i}$ , and the scattered intensity varies as  $\cos^2 2\theta$ , as a result of the projection  $\vec{E}_i \cdot \vec{E}_o$ . For X-rays, this independent dipole approximation is called kinematic scattering. This treatment of the polarization correction has been carried forward by many sources, including texts such such as Azároff [1955] and into more modern discussions such as Klug and Alexander [1974] figure 3-11 and equation 3-37, and Yao and Jinno [1982]. Azároff equation 15 gives the most commonly used form of the intensity variation due the combined effect of polarization from the powder specimen at diffraction angle  $2\theta_s$ and a monochromator/analyzer crystal at diffraction angle  $2\theta_{\rm m}$ :

$$I \propto 1 + \cos^2 2\theta_{\rm m} \cos^2 2\theta_{\rm s} \equiv \eta_{\rm dipole} , \qquad (1)$$

where we define  $\eta_x$  to be the "diffraction efficiency" for the particular configuration x.

In contrast, the theory of dynamical diffraction from a perfect crystal was first laid out by Darwin [1914] in papers which noted, but did not evaluate, the effects of weak absorption of X-rays in the crystal. Equation 12 of that paper includes the polarization term  $1 + |\cos 2\theta|$  for the intensity of reflection of broadband, unpolarized radiation from a perfect crystal. Many papers since have presented a more complete description: Prins [1930] first included absorption. A very detailed and mathematically complete description is Batterman and Cole [1964]. A modern, condensed presentation of the theory can be found in Authier [2010].

There is nearly complete unanimity on how this issue has been treated in data analysis; examples include He [2018], equation 6.64 and beyond and Lipson et al. [2006] equation 6.2.2.3 and the discussion in section 6.2.6, which is labeled as a discussion of single-crystal reflectors, but immediately introduces the mosaicity of the crystal, which limits the validity of the discussion to the case of a kinematically-reflecting mosaic crystal. While certain authors have used an approach based on dynamical scattering for analysis of data from single crystals, this work would not have been seen as being relevant to analyses of powder diffraction data. Examples include Kuriyama and Hosoya [1963] and Miyake et al. [1964]. A few papers have directly addressed this for powder diffraction, but without the inclusion of experimental data. Jennings [1981] is very comprehensive theoretically, but the only calculated result is for a graphite mosaic. In this case, the conclusion is that one really has to measure the correct polarization factor on a graphite crystal, since it depends strongly on the geometry and the characteristics of the crystal and radiation. Kerr and Ashmore [1974] equation 3 shows the correct result for the geometry we will describe. An IUCr survey Jennings [1984] does have some measurements cataloged, and recommends a purpose-designed polarimeter Le Page et al. [1979] as the definitive way to measure this. We have built such an instrument, but the difficulty of getting highly reliable measurements from it led us to instead carry out the direct comparisons we present below, since they are the most relevant and accessible to typical lab practice.

Recent work at the National Institute of Standards and Technology (NIST) has resulted in precise measurements of peak intensities from powder samples of well-understood materials, on an instrument with a Ge 111 Johansson [1933] incident beam monochromator (IBM), and on instruments with an unpolarized beam. When utilizing the Blake theory and its successors to correct for the IBM, analyses of these powder diffraction data showed reductions of nearly 10% of the expected intensity for reflections far from  $2\theta = 90^{\circ}$ , far outside any experimental uncertainties. The lack of any other credible source of uncertainty led us to evaluate the effect on the polarization due to the monochromator, and consequently to the understanding that the customary approach to polarization, relying on the kinematic scattering model, did not accurately account for the effect of dynamical scattering from a Ge Johansson IBM.

## 2 Dynamical Approach

In a nearly perfect single-crystal, the rocking curve width is of the order of tens of seconds of arc, and the divergence of the incident beam for typical laboratory diffractometers is generally at least two orders of magnitude greater than that. Thus, the rocking curve samples a segment of the spectrum of the incoming beam which has constant intensity. Thus, the diffracted intensity is proportional to the area under the rocking curve. The width  $\delta$  of the rocking curve (see, *e.g.*, equation 5.1.3.6 in Authier) can be written in simplified form as  $\delta = k C$ , where k is a collection of terms which do not depend on the polarization, and C is polarization-dependent. In the limit of a weakly absorbing crystal, the rocking curve has nearly unit height, resulting in the area being proportional to the width. The factor C is critical here, as it contains the polarization effect; for  $\sigma$  polarization,  $C_{\sigma} = 1$ , and for  $\pi$  polarization,  $C_{\pi} = |\cos 2\theta|$  (see figure 5.1.2.5 and discussion in Authier).

Since the factors absorbed in k are common between the two polarizations, and assuming the powder sample behaves as a kinematic scatterer, we can compute the diffracted intensity from the monochromator and powder system, of the initially unpolarized beam, as:

$$I \propto C_{\sigma} \eta_{s,\sigma} + C_{\pi} \eta_{s,\pi}$$
  
= 1 + |cos 2\theta\_m| cos<sup>2</sup> 2\theta\_s \equiv \eta\_{IBM}, (2)

where the symbols  $\eta_{s,\sigma}$  and  $\eta_{s,\pi}$  refer to the efficiency of scattering by the sample for each polarization,  $2\theta_m$  is the diffraction angle of the monochromator, and  $2\theta_s$  is the diffraction angle of the sample. In many references, the polarization correction is given a normalizing denominator, which is independent of the diffraction angle of the sample. Since all intensities are relative to each other in these measurements, the denominator changes nothing in the interpretation of the data, and it is omitted here.

A more complete treatment of this includes absorption effects in the crystal. We can compute the ratio of the areas of the respective rocking curves with and without absorption, using a code for calculating rocking curves based strictly on Batterman and Cole [1964], and described in Mendenhall et al. [2019]. We use as an example a germanium 111 monochromator diffracting copper  $K_{\alpha}$  radiation at a photon energy of 8047 eVat a Bragg angle of  $\theta_{\rm m} = 13.64^{\circ}$ . Note that, even though germanium is a strong X-ray absorber, the 111 reflection has very high extinction relative to this, and it can be considered a weak absorber for this discussion.

In figure 1 through 4, we display the results of these calculations. Figure 1 shows the Darwin case with no absorption. The angle scale is in seconds of arc offset from the Bragg angle; the offset from the center is due to the index of refraction of the germanium. The text shows the ratio of the areas of the two rocking curves, integrated out to  $\pm 250$  seconds of arc (1.2 mr) from the center. As indicated in the text, the resulting numerically determined area ratio is very close to  $\cos 2\theta$ . Figure 2 shows the fully realistic rocking curve with the known absorption of the germanium crystal included; the  $\pi/\sigma$  intensity ratio of 0.8785 is still quite close to



Figure 1: Rocking curves for a Ge-111 monochromator with copper  $K_{\alpha}$  radiation at 8047 eV. The quantity  $\pi/\sigma$  in the legend is the ratio of the numericallyintegrated areas of the rocking curves: No absorption (Darwin theory)



Figure 2: Rocking, with absorption (Darwin - Prins theory)

 $\cos 2\theta$ , but it is clear that there is a roughly 1% correction required to account for the effect of absorption. Note that the area ratio for a kinematic monochromator would be  $\cos^2 2\theta = 0.7899$ . Figures 3 and 4 show that the result does not depend strongly on the asymmetry angle of the monochromator; in practice Johann [1931]- and Johansson-type monochromators are often asymmetrical to achieve desired focusing properties.

#### 3 Measurements and Analysis

To test the thesis that the dynamical rocking curve integral is the appropriate correction to account for the







Figure 4: Rocking, with absorption, asymmetry  $= +3^{\circ}$ 

polarization effects of an IBM, we have compared the intensity of diffraction peaks measured on the NIST Divergent Beam Diffractometer (DBD) Cline et al. [2015] configured with a Ge 111 Johannson IBM and with no monochromator, and a commercial desktop diffractometer (Malvern Panalytical Aeris<sup>1</sup>) with no monochromator. Both systems used a nickel filter to remove  $K_{\beta}$  radiation when configured without a monochromator. We compare the results both from NIST Standard Reference Material (SRM) 1976c NIST [2019], a sintered alumina disk, and the feedstock for the upcoming NIST SRM 676b, a non-orienting corundum powder similar to SRM 676a NIST [2015]. Peak intensities were determined in two different ways: Fundamental Parameters Approach (FPA) Cheary and Coelho [1998a,b], Cheary et al. [2004], Mendenhall et al. [2015] fits, and the empirical split-Pearson-VII profile shape function, with 6 Chebyshev background parameters in both cases. In both cases, residuals were included, as per Mendenhall and Cline [2019], to get accurate peak areas independent of an exact fit. The fits were carried out in Topas 6 Bruker AXS [2017]. The two methods were completely consistent, so we only present the results of the FPA fits. Note one significant difference between SRM 1976c and SRM676b feedstock is that SRM1976c shows significant deviation in intensities from those of simple dynamical scattering due to extinction effects in the relative large crystallites of SRM1976c.

The polarization correction for the kinematic scattering from the sample is determined from either eq. 1 or eq. 2, using  $\theta_{\rm m} = 0$ , resulting in an intensity correction of

$$I \propto 1 + \cos^2 2\theta_{\rm s} \equiv \eta_{\rm unpol} \;.$$
 (3)

Since the certified values are measured on the DBD configured with the IBM, these values are then ad-

<sup>&</sup>lt;sup>1</sup>Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the U.S. government, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.



Figure 5: Ratio of intensity measured on partiallypolarized beam from the DBD with IBM to intensity measured with unpolarized beam on the Aeris instrument, as corrected with kinematic and dynamical theory: Results from SRM 676b feedstock.



Figure 6: Aeris vs. DBD; results from SRM 1976c

justed according to equation 2:

$$I_{\rm unpol} = \frac{\eta_{\rm unpol}}{\eta_{\rm IBM}} I_{\rm IBM} = I_{\rm IBM} \frac{1 + \cos^2 2\theta_{\rm s}}{1 + \cos 27.3^{\circ} \cos^2 2\theta_{\rm s}}$$
(4)

using the simplified, weak-absorption equation, or

$$I_{\rm unpol} = I_{\rm IBM} \frac{1 + \cos^2 2\theta_{\rm s}}{1 + 0.8785 \cos^2 2\theta_{\rm s}} \tag{5}$$

if the effects of absorption in the IBM are to be included. The difference between equations 4 and 5 is at most 0.5% for our system.

Figures 5 and 6 show the comparison between measurements made on the Aeris, with an unpolarized beam, and measurements made on the DBD, with the germanium monochromator, comparing the corrections based on both equation 1 and on equation 4. Figures 7 and 8 show the same result, comparing the DBD without the IBM to the DBD with the IBM. The corrected intensity ratio should be constant across the  $2\theta$  range. It is clear that the dynamical correction for the monochromator is a better representation of its true behavior.



Figure 7: Ratio of intensity measured on partiallypolarized beam from the DBD with IBM to intensity measured with unpolarized beam on the DBD with no IBM, as corrected with kinematic theory vs. dynamical theory: Results from SRM 676b feedstock.



Figure 8: DBD IBM vs. no-IBM; results from SRM 1976c

# 4 Rietveld Analysis of Powder Data

Lastly, Rietveld analyses of data from the SRM 676b alumina feedstock were performed to test for the impact of using the dynamically based polarization model on a structural analysis. The data were those to be used for the certification SRM 676b, as such there were 20 data sets collected on the DBD configured with the IBM. Again the FPA method, as implemented on TOPAS, was used for the analysis. Refined parameters that were considered as results were the mean values from 20 refinements of the 20 independent data sets. Typical results using dynamically based polarization model are illustrated in Figure 9. There was a slight reduction in the goodness-of-fit parameter between the two models, 1.108 for the dynamical vs. 1.124; not substantial but not insignificant. However, with regards to the structural parameters, they were nearly identical with two noteworthy exceptions. The thermal parameters of the Al atoms shifted by 3% with a corresponding 3% shift in the scale factor. While this may not amount to a substantial change in structure determinations, a 3% shift in scale factor values will strongly impact a quantitative Rietveld analysis.



Figure 9: Rietveld analysis of alumina, SRM 676b, using the dynamical scattering polarization model. Data collected on DBD configured with the Ge Johansson IBM.

#### 5 Discussion

The certification of NIST SRM 1976a & 1976b for powder diffraction required the precise determination of relative intensity values of the diffraction profiles over the full range of  $2\theta$  angle. Machines equipped with a Ge 111 Johansson IBM were used for collection of certification data owing to the reduced complexity of the profiles from such a machine. NIST then provided relative intensity values that were adjusted from the certified ones, using the classical models for the polarization correction. This permitted the use of the SRM on machines of differing optic configurations. However, in the course of certifying the next generation of this standard, SRM 1976c, we found persistent errors in the application of the SRM to machines of non-IBM configurations.

The long-accepted approach to account for the effects of polarization in powder diffraction has been found to be inappropriate when a "perfect" singlecrystal, such as a Ge 111 Johansson optic, is used as a monochromator. We have found that the error in relative intensities introduced by the kinematic approach can be as much as 10 % at its maxima far from a diffraction angle of  $2\theta_s = 90^\circ$  for 8 keV X-ray radiation on a monochromator with a 13.65° Bragg angle. Using dynamical theory for the monochromator reduces this discrepancy to less than 2%. This validates the application of dynamical theory to polarization effects from these monochromators.

We do note that some of the remaining error is clearly systematic, and that a lab striving for the highest possible intensity fidelity should be able to replicate our process, comparing their own monochromator to open beam, to obtain a slightly better correction than that derived directly from dynamical theory. The difference, though, is quite small, and we believe that it is most likely that the results we publish here will provide a high degree of accuracy without the effort and possible pitfalls of making that measurement.

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