

A note on the relation of anisotropic peak broadening with lattice symmetry in powder diffraction

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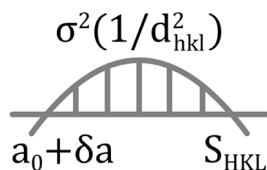
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A bridge is established between the Gregorkiewicz & Boschetti [*Acta Cryst.* (2024), **A80**, 439–445] and Stephens [*J. Appl. Cryst.* (1999), **32**, 281–289] formalisms of anisotropic peak broadening in powder diffraction. The paper by Gregorkiewicz & Boschetti presented formulas describing position shifts of low-symmetry peaks due to different lattice relaxation schemes. Anisotropic peak broadening caused by lattice relaxation can be parameterized by the variance of slightly dispersed peaks' positions. The calculated variances are compared with formulas from the widely used phenomenological model of anisotropic peak broadening by Stephens. Specific relations between anisotropic peak broadening parameters can be a hint of a possible unresolved peak splitting due to lattice symmetry lowering.

The paper by Gregorkiewicz & Boschetti (2024) presented formulas for the $1/d_{hkl}^2$ position of hkl contributions to the same (hkl) peak in a powder diffraction pattern considering six minimal lattice symmetry relaxation schemes: (1) cubic to tetragonal, (2) cubic to rhombohedral, (3) hexagonal to orthorhombic/monoclinic, (3a) hexagonal to orthorhombic, (4) tetragonal to orthorhombic, (5) orthorhombic to monoclinic, (6) monoclinic to anorthic (triclinic). Based on these formulas I calculated the variances $\sigma^2(h, k, l)$ of the $1/d_{hkl}^2$ values of the hkl contributions. For all relaxation schemes the variances $\sigma^2(h, k, l)$ are expressed as fourth-order polynomials in h, k, l indices:

$$\sigma^2(h, k, l) = \sum_{HKL} S_{HKL} h^H k^K l^L, \quad (1)$$

with $H + K + L = 4$. Symmetry restrictions for each Laue class for S_{HKL} coefficients were given by Popa (1998). A phenomenological model of anisotropic peak broadening (Stephens, 1999; Popa, 1998) assumes that each crystallite in a powder sample is in general triclinic and that only average lattice constants over the whole sample fulfil restrictions of a given lattice symmetry. In this approach S_{HKL} coefficients are linear combinations of covariance matrix elements, which describe a lattice constant distribution in the polycrystalline sample (see Stephens, 1999). For each of the lattice relaxation schemes (1–6) listed above, the barycentre shift $\Delta\langle 1/d_{hkl}^2 \rangle$, the variance $\sigma^2(h, k, l)$ of $1/d_{hkl}^2$ and the relations between S_{HKL} parameters are given in Table 1. The effective peak widths calculated in a Rietveld refinement depend on the instru-



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mental resolution function, on $\sigma^2(h, k, l)$ and on possible other effects, *e.g.* crystallite size effects *etc.* Without specifying the peakshape function one can say that the total peak width is monotonic with $\sigma^2(h, k, l)$.

The anisotropic peak broadening method is often used to improve the Rietveld refinement, but the values of the Stephens parameters S_{HKL} are not always discussed. The equalities between S_{HKL} parameters in Table 1 included in square brackets, *e.g.* $[S_{400} = S_{040} = S_{004}]$, are identical to those given by Stephens (1999). The relations between S_{HKL} parameters included in two neighbouring brackets, *e.g.* $S_{004} = -S_{220}$ (see cubic to tetragonal in Table 1) are additional restrictions due to the specific lattice relaxation scheme and they were not provided by Gregorkiewicz & Boschetti (2024). The equations in Table 1 form a bridge between the Gregorkiewicz & Boschetti (2024) and Stephens (1999) formalisms, giving the values of the S_{HKL} parameters in terms of lattice parameter increments. One has to keep in mind that definitions of anisotropic peak broadening parameters used in Rietveld refinement software do not always agree with the definitions from the Stephens (1999) paper. For a quantitative analysis of the S_{HKL} parameters one should refer to the documentation of the specific Rietveld refinement program in use.

Leineweber (2017) showed a relationship between anisotropic peak broadening parameters and the strain tensor within symmetry-related low-symmetry domain states. Applying his general formula [see equation 10 of Leineweber (2017)] to the cubic to tetragonal lattice relaxation scheme leads to the same relationship between S_{HKL} parameters as given for this scheme in Table 1 [see equation 17 of Leineweber (2017)].

The study of Leineweber (2017) points out that the high-symmetry model with anisotropic peak broadening parameters and the low-symmetry model with isotropic peak broadening frequently yield in Rietveld refinements similar agreement factors. Therefore the choice of the proper model should be made in combination with possibly available additional information. Statistically relevant non-zero values of S_{HKL} parameters fulfilling the relations given in Table 1 obtained in Rietveld refinement of powder diffraction data can be a signature of a possible unresolved peak splitting due to lattice symmetry lowering. It should be possible to implement an automatic check of this relationship in Rietveld analysis software, which will alert the user to when there are grounds to consider a low-symmetry lattice model. Users could also manually constrain S_{HKL} parameters to follow equalities given in Table 1.

Additional remark: in the Gregorkiewicz & Boschetti (2024) supporting information I found an error in the equations of barycentre shift for relaxation from cubic to rhombohedral and from orthorhombic to monoclinic. Instead of $B_r = (h^2 + k^2 + l^2) \sin \delta\alpha$ and $B_m = (h^2/a^2 + k^2/b^2) \sin \delta\gamma$, it should be $B_r = 2a^{-2}(h^2 + k^2 + l^2) \sin^2 \delta\alpha + O(\sin^3 \delta\alpha)$ and $B_m = (h^2/a^2 + k^2/b^2) \tan^2 \delta\gamma$, respectively.

Table 1

Number of split peaks for general (hkl) , values of barycentre shift $\Delta(1/d_{hkl}^2)$ within linear approximation, variances $\sigma^2(h, k, l)$ of dispersed $1/d_{hkl}^2$ positions within quadratic approximation and relations between anisotropic peak broadening parameters S_{HKL} as defined by Stephens (1999) for all relaxation schemes discussed by Gregorkiewicz & Boschetti (2024).

1. Cubic to tetragonal (3 peaks) $c = a + \delta a$ $\Delta(1/d_{hkl}^2) = -\frac{2}{3}a^{-2}(h^2 + k^2 + l^2)(\delta a/a)$ $\sigma^2(h, k, l) = \frac{8}{9}a^{-4}(h^4 + k^4 + l^4 - h^2k^2 - h^2l^2 - k^2l^2)(\delta a/a)^2$ $[S_{400} = S_{040} = S_{004}] = [-S_{220} = -S_{202} = -S_{022}] = \frac{8}{9}a^{-4}(\delta a/a)^2$ (HHH) , locally narrowest; $(H00)$, locally broadest
2. Cubic to rhombohedral (4 peaks) $\alpha = (\pi/2) + \delta\alpha$ $\Delta(1/d_{hkl}^2) = 0$ $\sigma^2(h, k, l) = 4a^{-4}(h^2k^2 + h^2l^2 + k^2l^2)(\delta\alpha)^2$ $[S_{220} = S_{202} = S_{022}] = 4a^{-4}(\delta\alpha)^2$ and $[S_{400} = S_{040} = S_{004}] = 0$ $(H00)$, locally narrowest; (HHH) , locally broadest
3. Hexagonal to orthorhombic/monoclinic (6 peaks) $b = a + \delta a$ and $\gamma = (2\pi/3) + \delta\gamma$ $\Delta(1/d_{hkl}^2) = -\frac{4}{3}a^{-2}(h^2 + hk + k^2)[(\delta a/a) - \frac{\sqrt{3}}{3}\delta\gamma]$ $\sigma^2(h, k, l) = \frac{32}{27}a^{-4}(h^2 + hk + k^2)^2[(\delta a/a)^2 + (\delta\gamma)^2]$ $[S_{400} = S_{040} = S_{310}/2 = S_{130}/2 = S_{220}/3] = \frac{32}{27}a^{-4}[(\delta a/a)^2 + (\delta\gamma)^2]$ $[S_{202} = S_{022} = S_{112}] = [S_{004}] = [S_{301}/2 = -S_{031}/2 = S_{211}/3 = -S_{121}/3] = 0$ $(00L)$, locally narrowest; (HKL) , locally broadest
3a. Hexagonal to orthorhombic (3 peaks) $\cos \gamma = -(a/2b)$ and $b = a + \delta a$ $\Delta(1/d_{hkl}^2) = -\frac{16}{9}a^{-2}(h^2 + hk + k^2)(\delta a/a)$ $\sigma^2(h, k, l) = \frac{128}{81}a^{-4}(h^2 + hk + k^2)^2(\delta a/a)^2$ $[S_{400} = S_{040} = S_{310}/2 = S_{130}/2 = S_{220}/3] = \frac{128}{81}a^{-4}(\delta a/a)^2$ $[S_{202} = S_{022} = S_{112}] = [S_{004}] = [S_{301}/2 = -S_{031}/2 = S_{211}/3 = -S_{121}/3] = 0$ $(00L)$, locally narrowest; (HKL) , locally broadest
4. Tetragonal to orthorhombic (2 peaks) $b = a + \delta a$ $\Delta(1/d_{hkl}^2) = -a^{-2}(h^2 + k^2)(\delta a/a)$ $\sigma^2(h, k, l) = a^{-4}(h^2 - k^2)^2(\delta a/a)^2$ $[S_{400} = S_{040}] = [-2S_{220}] = a^{-4}(\delta a/a)^2$ $[S_{004}] = [S_{202} = S_{022}] = 0$ (HHL) , locally narrowest; $(H0L)$, locally broadest
5. Orthorhombic to monoclinic (2 peaks) $\gamma = (\pi/2) + \delta\gamma$ $\Delta(1/d_{hkl}^2) = 0$ $\sigma^2(h, k, l) = 4a^{-2}b^{-2}h^2k^2(\delta\gamma)^2$ $[S_{220}] = 4a^{-2}b^{-2}(\delta\gamma)^2$ $[S_{400}] = [S_{040}] = [S_{004}] = [S_{202}] = [S_{022}] = 0$ $(H0L)$, $(0KL)$, locally narrowest; (HKL) , locally broadest
6. Monoclinic to anorthic (triclinic) (2 peaks) $\alpha = (\pi/2) + \delta\alpha$ and $\beta = (\pi/2) + \delta\beta$ $\Delta(1/d_{hkl}^2) = 0$ $\sigma^2(h, k, l) = 4l^2c^{-2}\cos^{-4}\gamma[a^{-1}(\delta\beta - \delta\alpha\cos\gamma)h + b^{-1}(\delta\alpha - \delta\beta\cos\gamma)k]^2$ $a^2(\delta\beta - \delta\alpha\cos\gamma)^{-2}[S_{202}] = b^2(\delta\alpha - \delta\beta\cos\gamma)^{-2}[S_{022}] = \frac{1}{2}ab(\delta\alpha - \delta\beta\cos\gamma)^{-1}(\delta\beta - \delta\alpha\cos\gamma)^{-1}[S_{112}] = 4c^{-2}\cos^{-4}\gamma$ $[S_{400}] = [S_{040}] = [S_{004}] = [S_{220}] = [S_{310}] = [S_{130}] = 0$ $(HK0)$ and $(00L)$, locally narrowest

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