FOUNDATIONS
ADVANCES

Volume 78 (2022)

Supporting information for article:

Effects of Voigt diffraction peak profiles on the pair distribution function

Jonas Beyer, Nikolaj Roth and Bo Brummerstedt Iversen

S1. Refinement results for Ni

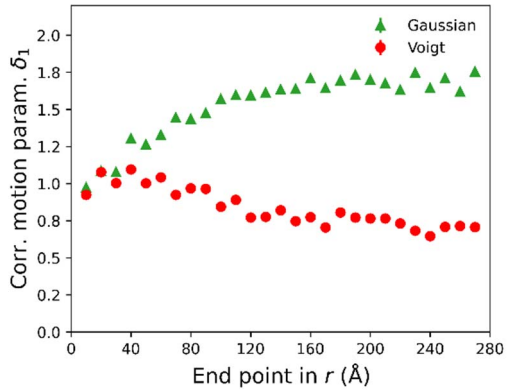
The refinement results for the PXRD and the two PDF refinements are summarized in the table below.

Table S1 Refinement results of the reciprocal- and direct-space Rietveld refinements. *The lattice parameter was fixed to the value found from the full-range PDF Voigt model refinement.

	PXRD (Rietveld refinement)	PXRD (Rietveld refinement with fixed lattice param.)	PDF Voigt	PDF Gaussian (*PDFgui)*
R_{wp}	4.90%	4.91%	8.59%	12.34%
Scale	0.04363(6)	0.04364(6)	0.1796(2)	0.1542(2)
a [Å]	3.52430(2)	3.52417*	3.52417(1)	3.52417(1)
B_{iso} [Å^2]	0.249(1)	0.249(1)	0.265(1)	0.335(2)
δ_1 [Å]	--		0.614(6)	1.707(8)
δ_G^*	0.00249(1)	0.00250(1)	0.00163(1)	--
δ_L^*	0.00231(1)	0.00231(1)	0.00282(1)	--
Q_{damp}				0.00497(3)
Q_{broad}				0.0175(1)
$\sin\theta$ shift	0.0021(2)	0.0033(1)		

S2. PDF refinement results for models with varying ranges

Refinement results from the Gaussian (filled green triangles) and Voigt (filled red circles) models for the correlated motion parameter are shown below in Figure S1.



S3. Approximation of the full-width half-maximum of a Voigt function

The full-width half-maximum (FWHM), Γ_V , of a Voigt function can be approximated with (Olivero & Longbothum, 1977)

$$\Gamma_V = 0.5346\,\Gamma_L + \sqrt{0.2166\,\Gamma_L^2 + \Gamma_G^2}$$

, where Γ_G and Γ_L are the Gaussian and Lorentzian FWHM, respectively. These are related to the 'standard deviation' and HWHM through the following

$$\Gamma_G = 2\sqrt{2\ln(2)}\sigma_G$$

$$\Gamma_L = 2\gamma_L$$

In the case of a linearly broadened Lorentzian peak profile function ($\delta_L > 0,\ K_G, K_L, \delta_G = 0$), the FWHM of the resulting PDF peaks will be

$$\Gamma_V = 1.0692\,\delta_L r_0 + \sqrt{0.8664\,\delta_L^2\,r_0^2 + 8\ln(2)\sigma_{r,0}^2}$$

, where $\sigma_{r,0}$ is the 'intrinsic' PDF peak width from the Debye-Waller factor and r_0 is the PDF peak position. The FWHM Voigt parameters K_G^*, K_L^*, δ_G^*, and δ_L^* are simply defined as

$$K_G^* = 2\sqrt{2\ln(2)}K_G, \qquad K_L^* = 2K_L$$

$$\delta_G^* = 2\sqrt{2\ln(2)}\delta_G, \qquad \delta_L^* = 2\delta_L$$

S4. Definition of the Thompson-Cox-Hastings pseudo-Voigt peak profile function

The Thompson-Cox-Hasting pseudo-Voigt was first defined in 1987 (Thompson *et al.*, 1987).The main proposition was to parameterize the pseudo-Voigt function Ω_{pV} using the Gaussian and Lorentzian FWHM, Γ_G and Γ_L respectively, rather than the customary total FWHM parameter and mixing parameter, Γ and η, respectively. The general expression for the pseudo-Voigt is

$$\Omega_{pV}(x,\eta,\Gamma) = \eta\, L(x,\Gamma) + (1-\eta)\, G(x,\Gamma)$$

$$L(x,\Gamma) = \frac{2}{\pi\Gamma}\frac{1}{1+\frac{4x^2}{\Gamma^2}}, \qquad G(x,\Gamma) = \frac{2}{\Gamma}\sqrt{\frac{\ln 2}{\pi}}\exp\left(-4\ln 2\frac{x^2}{\Gamma^2}\right)$$

Upon parameterization with Γ_G and Γ_L, the following numerical approximations to Γ and η were used

$$\Gamma^5 = \Gamma_G^5 + 2.69269\,\Gamma_G^4\Gamma_L + 2.42843\,\Gamma_G^3\Gamma_L^2 + 4.45163\,\Gamma_G^2\Gamma_L^3 + 0.07842\Gamma_G\Gamma_L^4 + \Gamma_L^5$$

$$\eta = 1.36603\frac{\Gamma_L}{\Gamma} - 0.47719\left(\frac{\Gamma_L}{\Gamma}\right)^2 + 0.11116\left(\frac{\Gamma_L}{\Gamma}\right)^3$$

Originally, the FWHM angular dependencies consisted of four parameters (*U*, *V*, *W*, and *X*). The modern formulation have two more (*Z* and *Y*), which brings the total to six parameters, given as

$$\Gamma_G^2 = U\tan^2\theta + V\tan\theta + W + Z/\cos^2\theta$$

$$\Gamma_L = X\tan\theta + Y/\cos\theta$$

The Voigt description used in this study only contains four parameters (K_G, K_L, δ_G, and δ_L), which correspond to *Z*, *Y*, *U*, and *X*, respectively. The reason for not using *W* is that using the three Gaussian parameters *U*, *W*, and *Z* simultaneously will result in a redundant description due to the trigonometric relation $\frac{1}{\cos^2 x} - \tan^2 x = 1$. Applying *U* and *Z* simultaneously will thus describe a constant broadening, leaving the *W* parameter obsolete. The reason for not using *V* is that it has a peculiar reciprocal space dependency, which causes very difficult integrals to emerge during Fourier transformation. In addition, in the experience of the authors, the *V* parameter is often highly correlated with the *U* parameter, meaning that only one should be employed in a structural model. However, this may be highly dependent on the experimental setup used for data collection.

The four TCH parameters *Z*, *Y*, *U*, and *X* are directly related to the FWHM Voigt parameters K_G^*, K_L^*, δ_G^*, and δ_L^* through the following equations, where the TCH parameters should be entered in radians

$$K_G^* = \frac{2\pi}{\lambda}\sqrt{Z}, \qquad K_L^* = \frac{2\pi}{\lambda}Y$$

$$\delta_G^* = \frac{1}{2}\sqrt{U}, \qquad \delta_L^* = \frac{1}{2}X$$

S5. TOPAS-Academic v6 Macros

Implementation of a Voigt peak profile function in *TOPAS* is achieved by selecting a pseudo-Voigt function using *peak type pv* and applying the keyword *more_accurate_Voigt* (TOPAS-Academic Version 6 Technical Reference, September 2016, p. 43). The code used in this study is shown below. Notice that the parameters KG, KL, deltaG, and deltaL are defined to describe the reciprocal-space FWHM of the Gaussian and Lorentzian contributions even though the refinements were carried out in angular space.

```
peak_type pv
                pv_lor  0
        pv_fwhm  1e-10

prm KG  0.001
prm deltaG  0.001

prm KL 0.001
prm deltaL  0.001

macro fwhm_gauss { Sqrt((lambda/(2*Pi)*KG*180/Pi)^2/Cos(Th)^2 + (2*deltaG*180/Pi)^2*Tan(Th)^2) }
macro fwhm_lor { lambda/(2*Pi)*KL*(180/Pi)/Cos(Th) + 2*deltaL*(180/Pi)*Tan(Th) }

gauss_fwhm = fwhm_gauss;
lor_fwhm = fwhm_lor;
more_accurate_Voigt
```

To model the effects of K_G, K_L, δ_G or δ_L on the PDF, the following macros in *TOPAS* have been employed. These are heavily inspired by macros dQ_damping, dQ_lor_damping and convolute_alpha found in the 'pdf.inc' file written by Dr. Phil Chater. The parameters KG, KL, deltaG, and deltaL has been defined such that they describe the FWHM of the peak shape function. This was chosen to ensure comparability with the reciprocal-space parameters as defined in the peak type above.

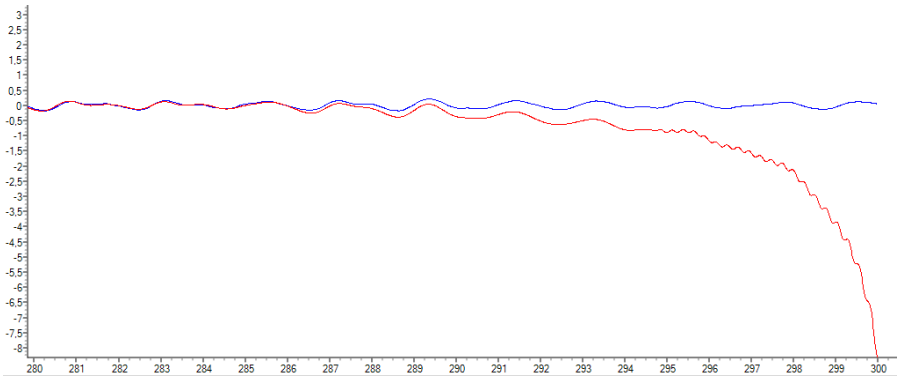
```
macro gauss_damp(KG,KGv)
{
        #m_argu KG
        If_Prm_Eqn_Rpt(KG, KGv, min 0.000001 max 1.0, del 0.0001)

        scale_phase_X = Exp(-0.5/(8*Ln(2))*(CeV(KG,KGv))^2 X^2);
}
```

```
macro lor_damp(KL,KLv)
{
        #m_argu KL
        If_Prm_Eqn_Rpt(KL, KLv, min 0.000001 max 1.0, del 0.0001)

        scale_phase_X = Exp(-0.5 CeV(KL, KLv) X);
}
```

```
macro gauss_broad(deltaG, deltaGv)
{
        #m_argu deltaG
        If_Prm_Eqn_Rpt(deltaG, deltaGv, min 0.000001 max 10 del 0.0001)

        local #m_unique fwhm = CeV(deltaG,deltaGv)*Xo;

  pdf_convolute = Exp(-4*Ln(2)/fwhm^2 X^2);
        min_X = Min(-10*fwhm, 0) ;
        max_X = Max(10*fwhm, 0) ;
        convolute_X_recal = If(Xo,1,1) 1;
}
```

```
macro lor_broad(deltaL, deltaLv)
{
        #m_argu deltaL
        If_Prm_Eqn_Rpt(deltaL, deltaLv, min 0.000001 max 10 del 0.0001)

        local #m_unique fwhm = CeV(deltaL, deltaLv)*Xo;

        pdf_convolute = fwhm/2/(X^2 + fwhm^2/4);
                min_X = Min(-10*fwhm, 0);
                max_X = Max(10*fwhm, 0);
                convolute_X_recal = If(Xo,1,1) 1;
}
```

The two latter macros have some issues concerning the way that *TOPAS* handles convolutions through the convolute_X_recal keyword. When *Xo* is is close to the maximum X value of the data set, the model will deviate significantly from the data set, as shown by the figure below. The blue line is the data set and the red line is the model. The data set in this example has data points up to 500 Å but the model is set to terminate at 300 Å. The deviation becomes more severe when the model range is increased.



A hotfix to this issue is to choose a longer range than necessary for the model refinement and then 'weighting out' the extra range by choosing an appropriate weighting scheme. In the following example, the model will be refined on a range up to 300 but will only be weighted by data points up to 250 by the following lines of code.

```
macro maxX {300}
weighting = If(Abs(X) < 250, 1, 0);

start_X   1.0
finish_X  maxX
```

The model using Q_{damp} and Q_{broad} was refined using the following macro, which mimics the algorithm used in *PDFgui*. The value of Q_{damp} was refined using the *dQ_damping* macro in the *pdf.inc* file.

```
macro Biso_Qbroad_Corr1_PDFgui(Biso, Bisov, Qbroad, Qbroadv, Delta, Deltav)
{
        #m_argu Biso
        #m_argu Qbroad
        #m_argu Delta
        If_Prm_Eqn_Rpt(Biso, Bisov, min 0.000 max 10.0, del 0.0001)
        If_Prm_Eqn_Rpt(Qbroad, Qbroadv, min -10 max 10 del 0.0001)
        If_Prm_Eqn_Rpt(Delta, Deltav, min -10 max 10 del 0.0001)


        beq = CeV(Biso,Bisov)*(1 + CeV(Qbroad,Qbroadv)^2*X^2 - CeV(Delta,Deltav)/X);
}
```

Supporting Information References

Olivero, J. & Longbothum, R. (1977). *J. Quant. Spectrosc. Radiat. Transfer* 17, 233–236.