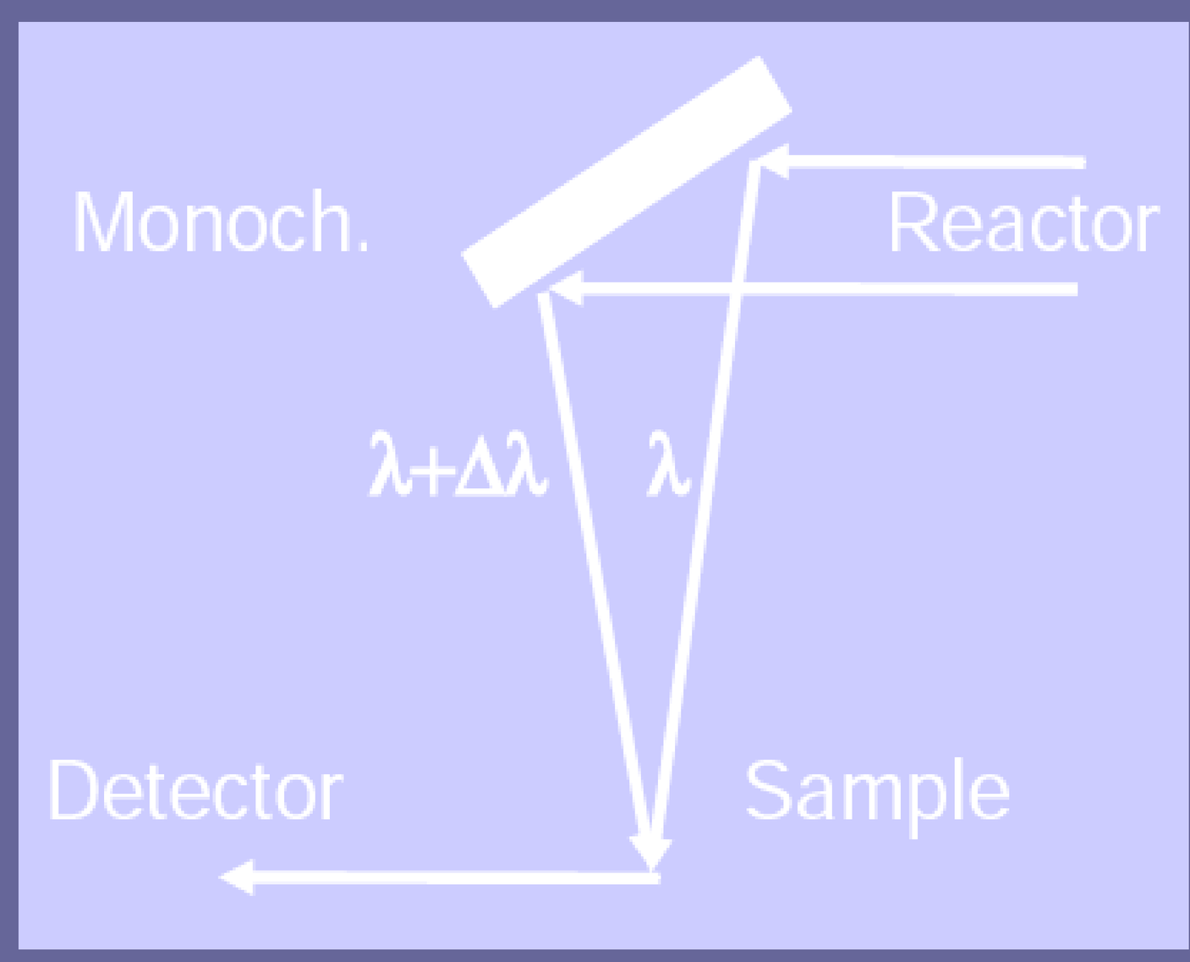
R-space effects of Q-space resolution: Deconvolution of neutron diffraction data from a reactor source

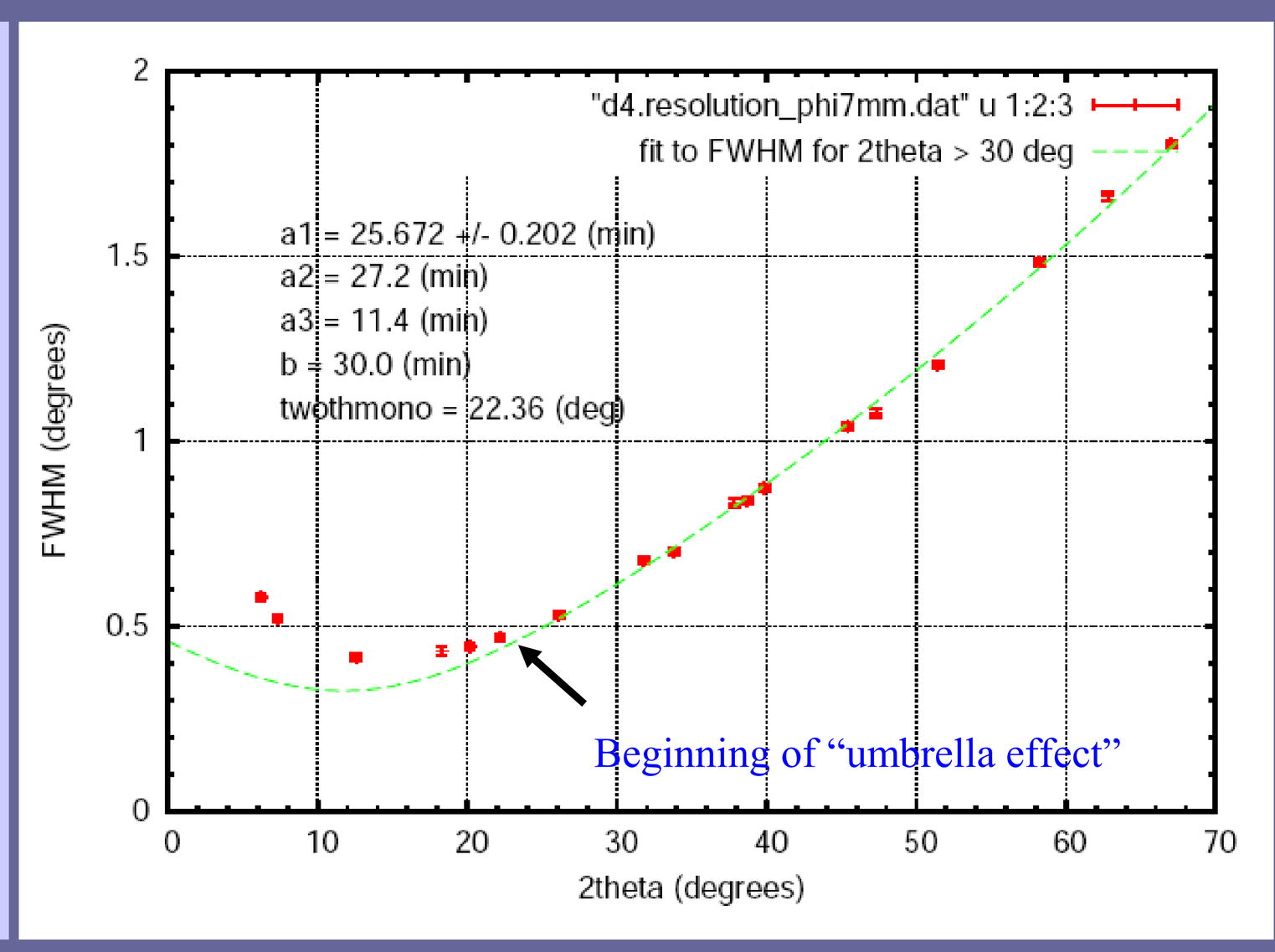
H.E. Fischer[1], **W.S. Howells**[2], **P.S. Salmon**[3]

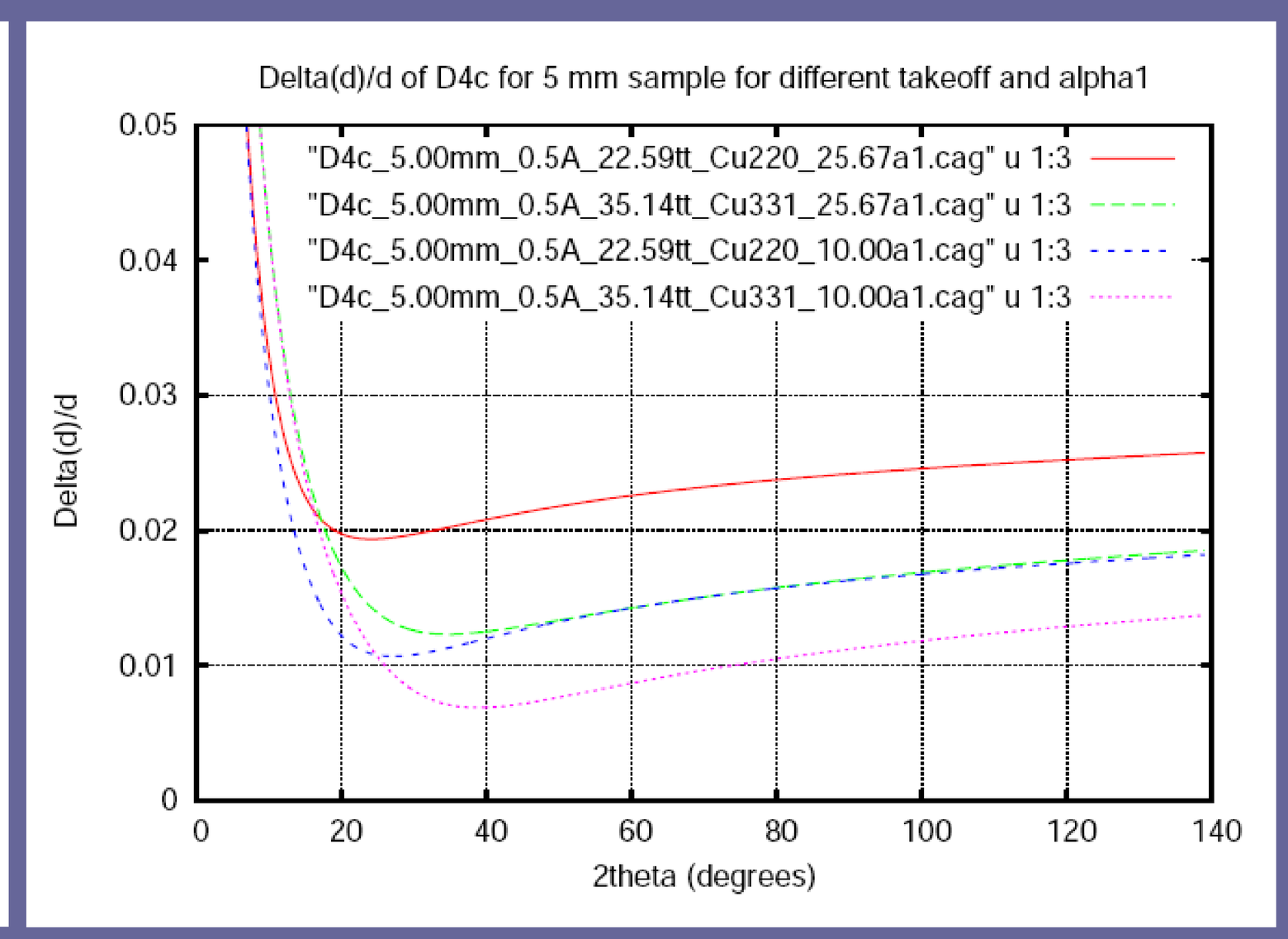
[1]*Institut Laue-Langevin, France* [2]*ISIS Facility, RAL, U.K.* [3]*University of Bath, U.K.*

For a reactor-source neutron diffractometer: The +/- scattering geometry leads to "Q-space focussing" that improves the FWHM of Bragg peaks and the resolution: $\Delta d/d = \Delta Q/Q = \Delta\theta \cdot ctg(\theta)$ where 2θ is the diffraction angle. The 2θ-dependence of $\Delta\theta$ is described by coefficients U, V and W [1,2]; e.g: U,V,W = 9.3805,-1.9033, 0.2029 for one of the standard configurations (0.5 A, Cu220, ϕ5mm sample) of the ILL's D4c diffractometer for liquids and glasses.

[1] G. Caglioti, et al, *Nucl. Instrum.* **3** (1958) 223-228.
[2] A.W. Hewat, *Nucl. Instrum. Methods* **127** (1975) 361-370.

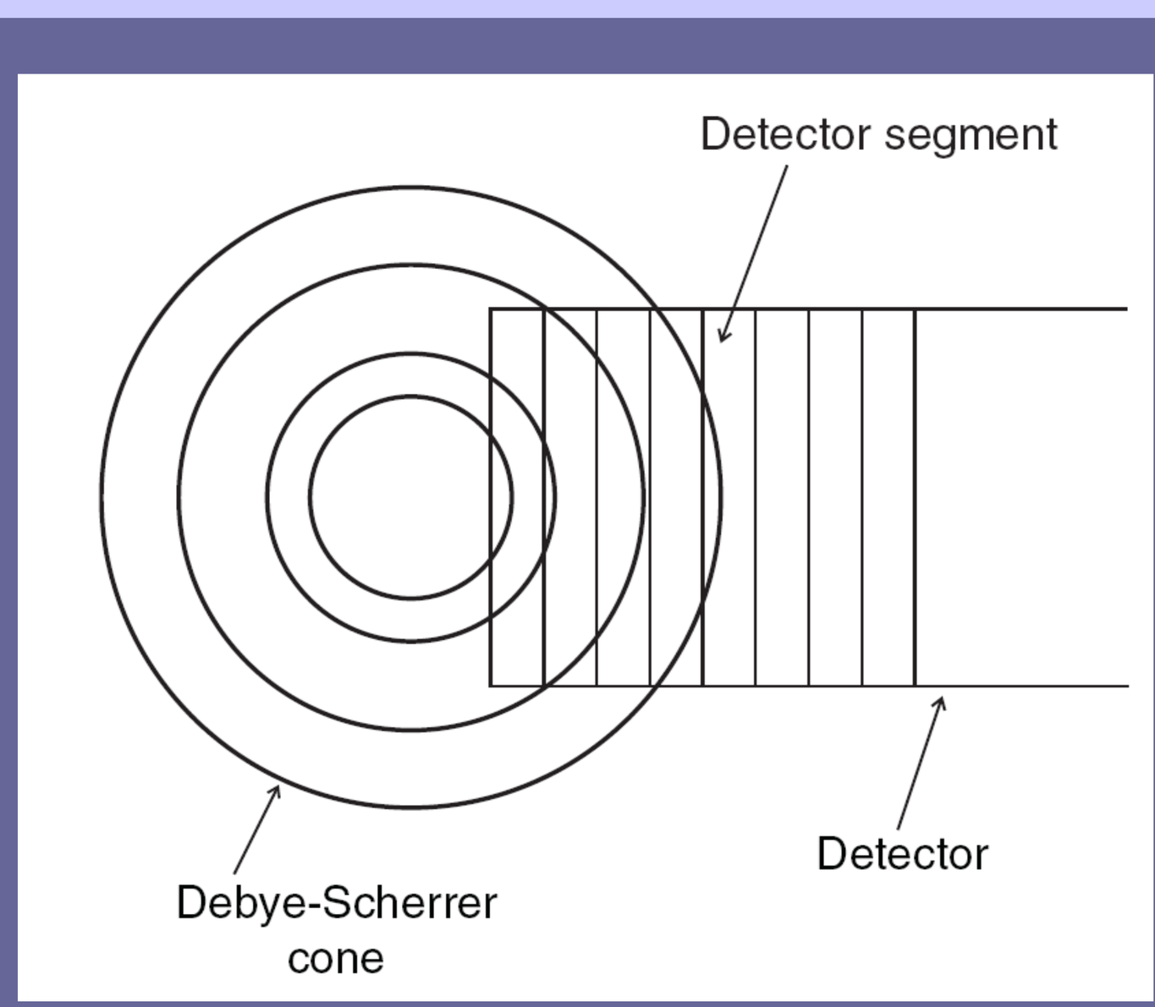


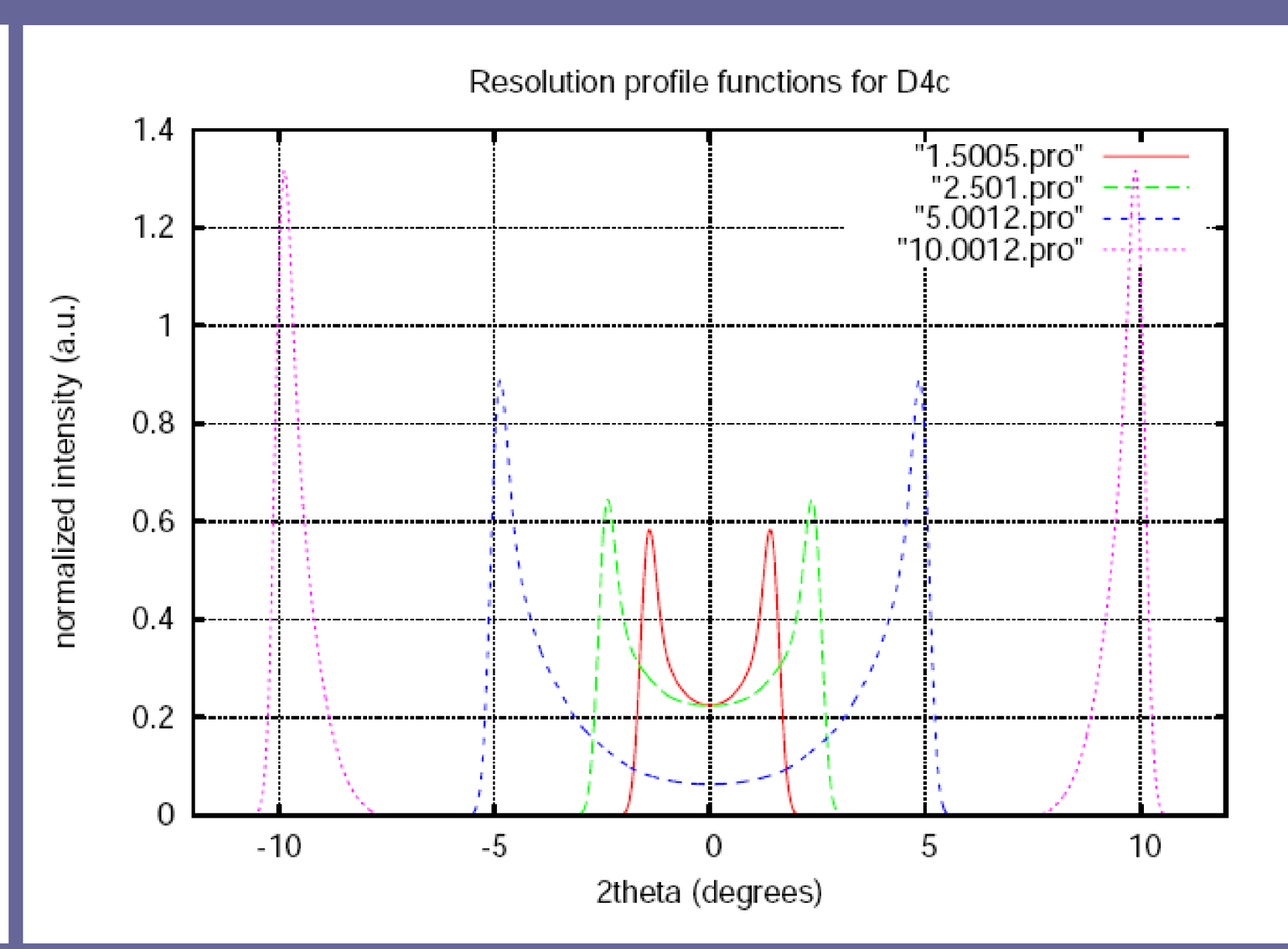


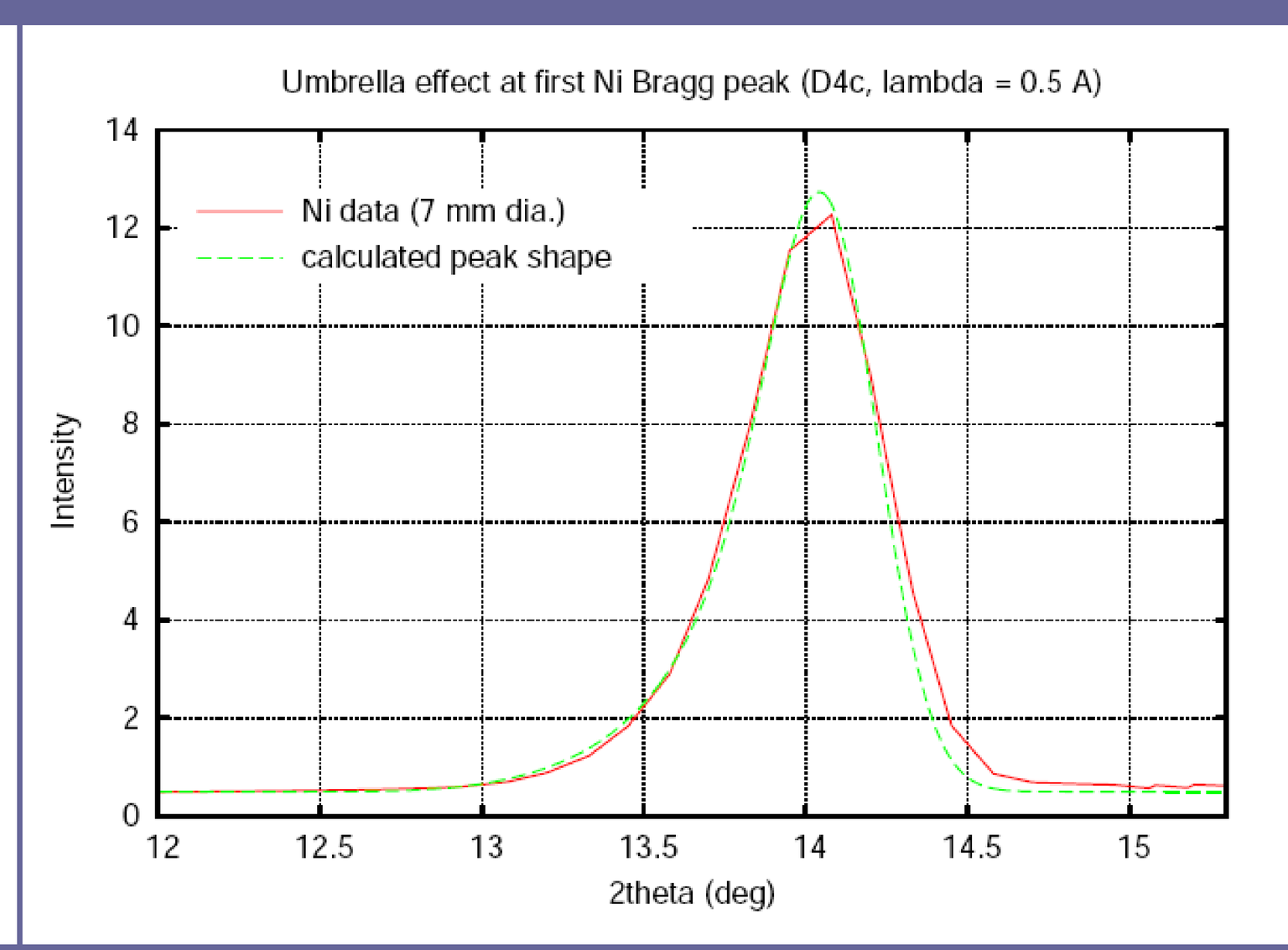


The "umbrella effect": At small diffraction angle 2θ, the diameter of Debye-Scherrer rings becomes comparable to, or smaller than, the detector-cell height of a 1-D position sensitive detector, leading to a modification of the Lorentz factor [3] and to an asymmetry+shift in the Bragg peak profile [4,5] that should be included in Rietveld refinement.

[3] M.J. Cooper and A.V. Glasspool, *J. Appl. Cryst.* **9** (1976) 63-67.
[4] B. van Laar and W.B. Yelon, *J. Appl. Cryst.* **17** (1984) 47-54.
[5] L.W. Finger, D.E. Cox and A.P. Jephcoat, *J. Appl. Cryst.* **27** (1994) 892-900.







General deconvolution of the 1-D diffraction pattern: Although a detector of 2-D sensitivity permits following or "straightening" the Debye-Scherrer rings, this only corrects for the umbrella effect, and not for other resolution effects coming from sample size, incident beam dispersion and detector resolution. In addition, diffraction data for liquids and glasses cannot be Rietveld-refined since there is no spatial periodicity, and since the diffraction peaks are of intrinsic width and not resolution-limited. Finally, no FT deconvolution tricks are possible because the resolution function depends on 2θ. In the general case then, the measured intensity $I(2\theta)$ can be written as a convolution of the true intensity $S(2\theta)$:

$I(2\theta) = Int[\,R(\rho,2\theta)\;S(2\theta-\rho)\,d\rho\,]$ where $R(\rho,2\theta)$ is the profile or resolution function at diffraction angle 2θ.

A Taylor's expansion of $S(2\theta-\rho)$ about 2θ and integration of each term leads to the moments of $R(\rho,2\theta)$:

$M_n(2\theta) = (1/n!) \cdot Int[\,(-\rho)^n\; R(\rho,2\theta)\,d\rho\,]$ which can be normalised as $A_n = M_n/M_0$ and $J(2\theta) = I(2\theta)/M_0$.

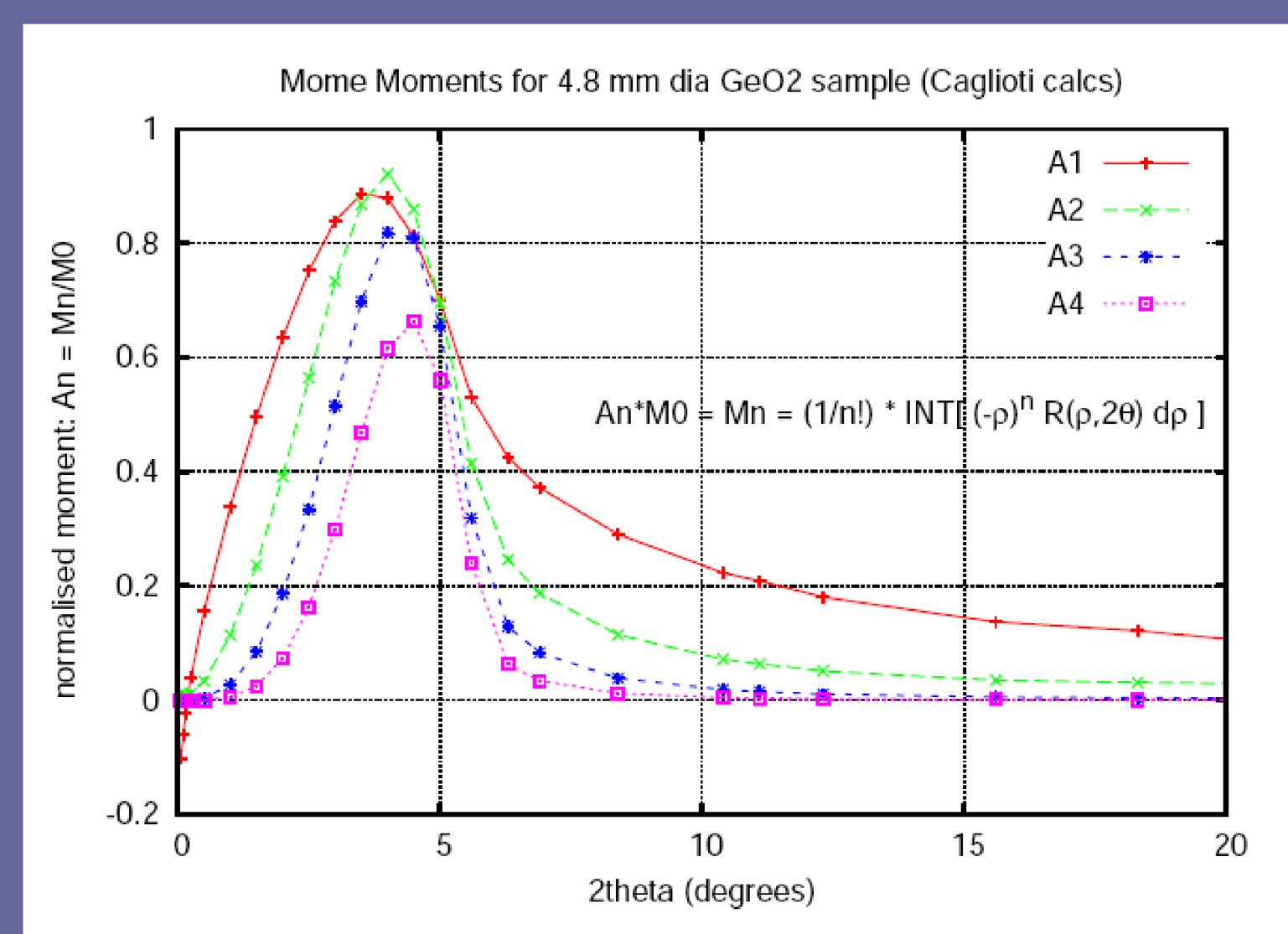
For M_n locally constant w.r.t. 2θ and considering only the first 4 derivatives of J w.r.t. 2θ, we derive:

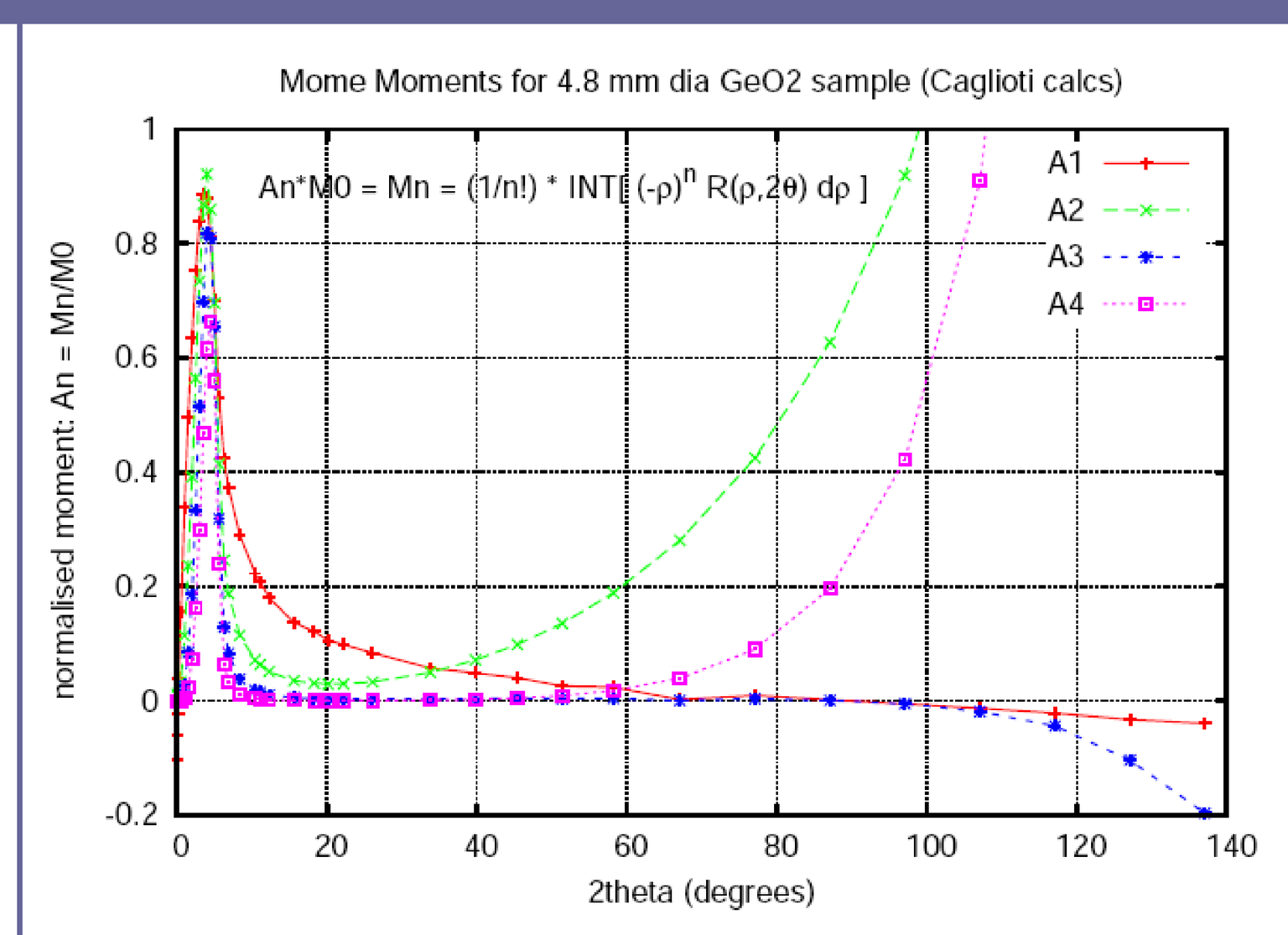
$S = J + c_1 J' + c_2 J'' + c_3 J''' + c_4 J''''$ where the correction coefficients c_n are given by:

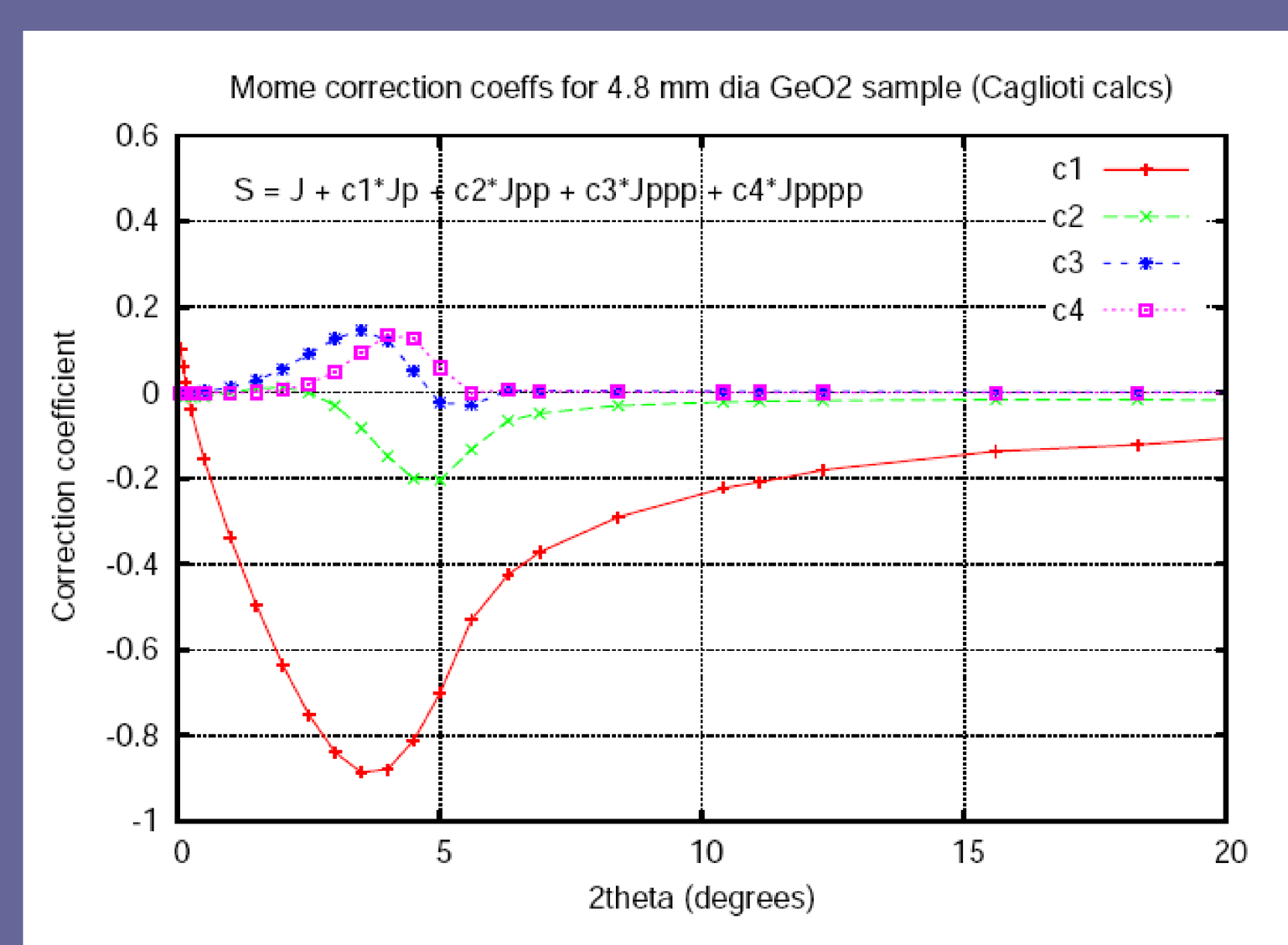
$c_1 = -A_1$ $\quad c_2 = -A_2 + A_1^2$ $\quad c_3 = -A_3 + 2A_1A_2 - A_1^3$ $\quad c_4 = -A_4 + 2A_1A_3 + A_2^2 - 3A_1^2A_2 + A_1^4$

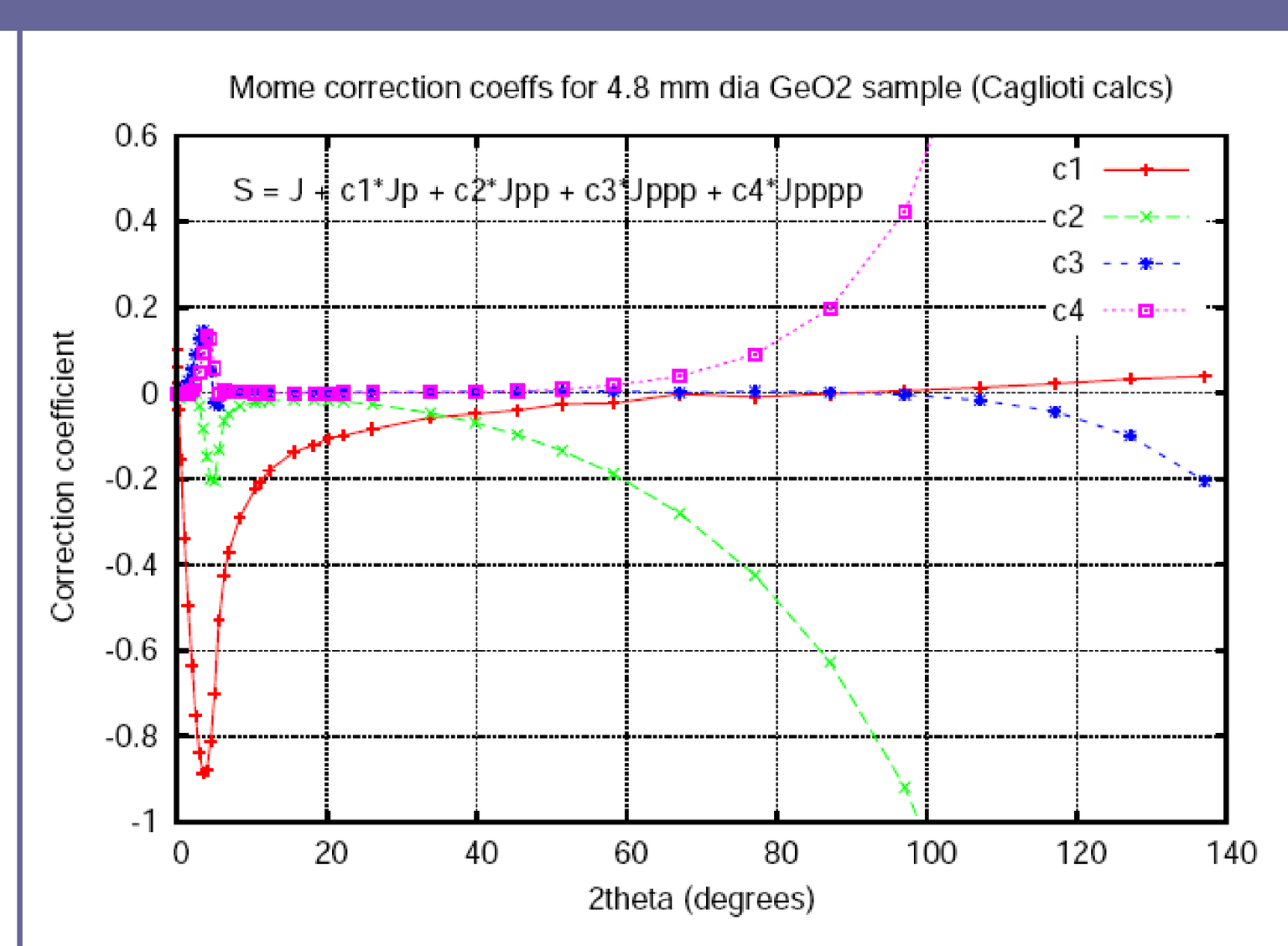
This "moments method" [6] of general deconvolution has already been applied to data for liquid Li [7] as well as for liquid and glassy $ZnCl_2$ [8], among other samples. Our software is named Decon.

[6] W.S. Howells, *Nucl. Instrum. Methods Phys. Res.* **219** (1984) 543-552.
[7] P.S. Salmon, et al, *J. Phys. Condens. Matter* **16** (2004) 195-222 (appendix).
[8] A. Zeidler, et al, *Phys. Rev. B* **82** (2010) 104208.

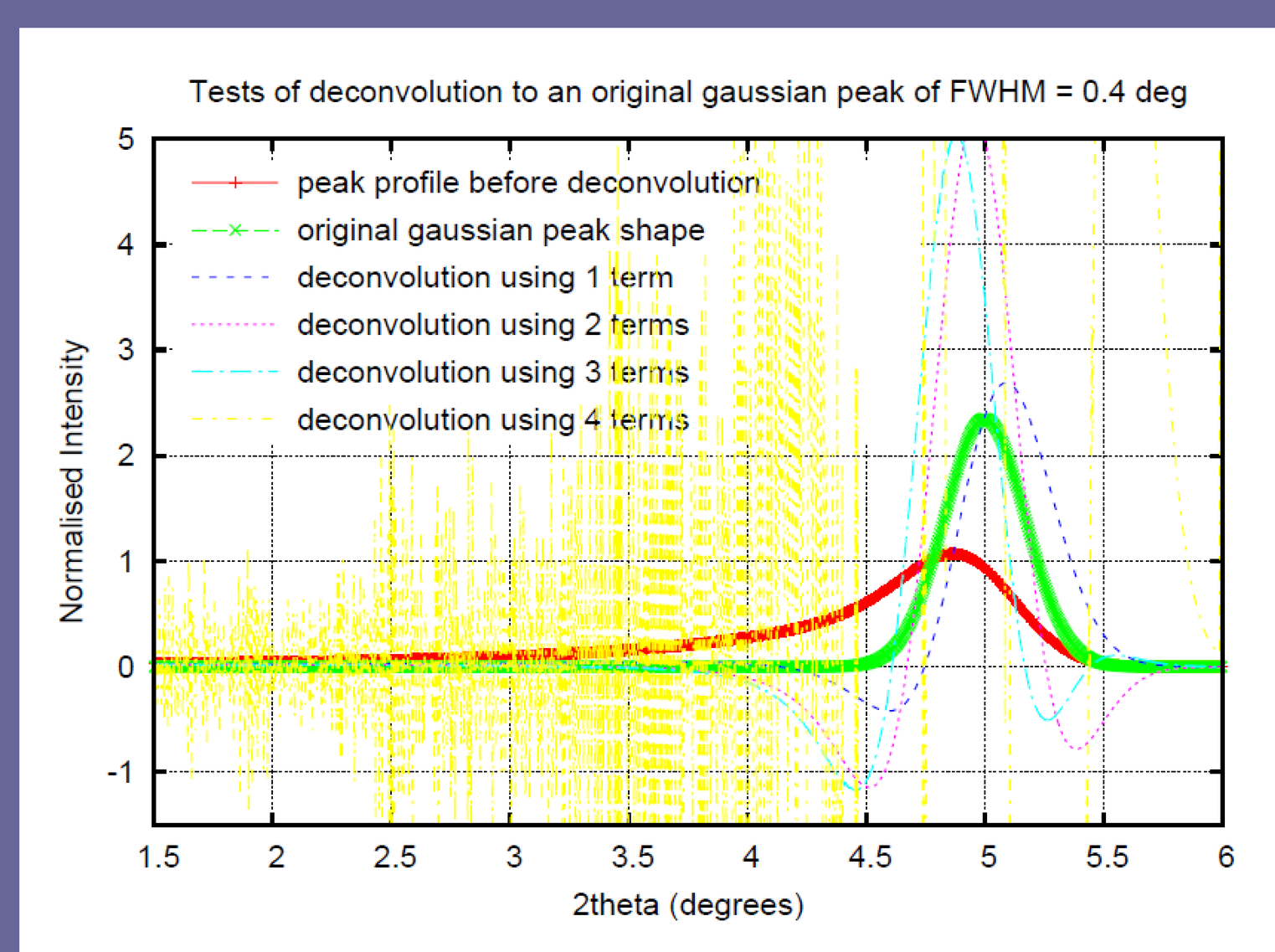


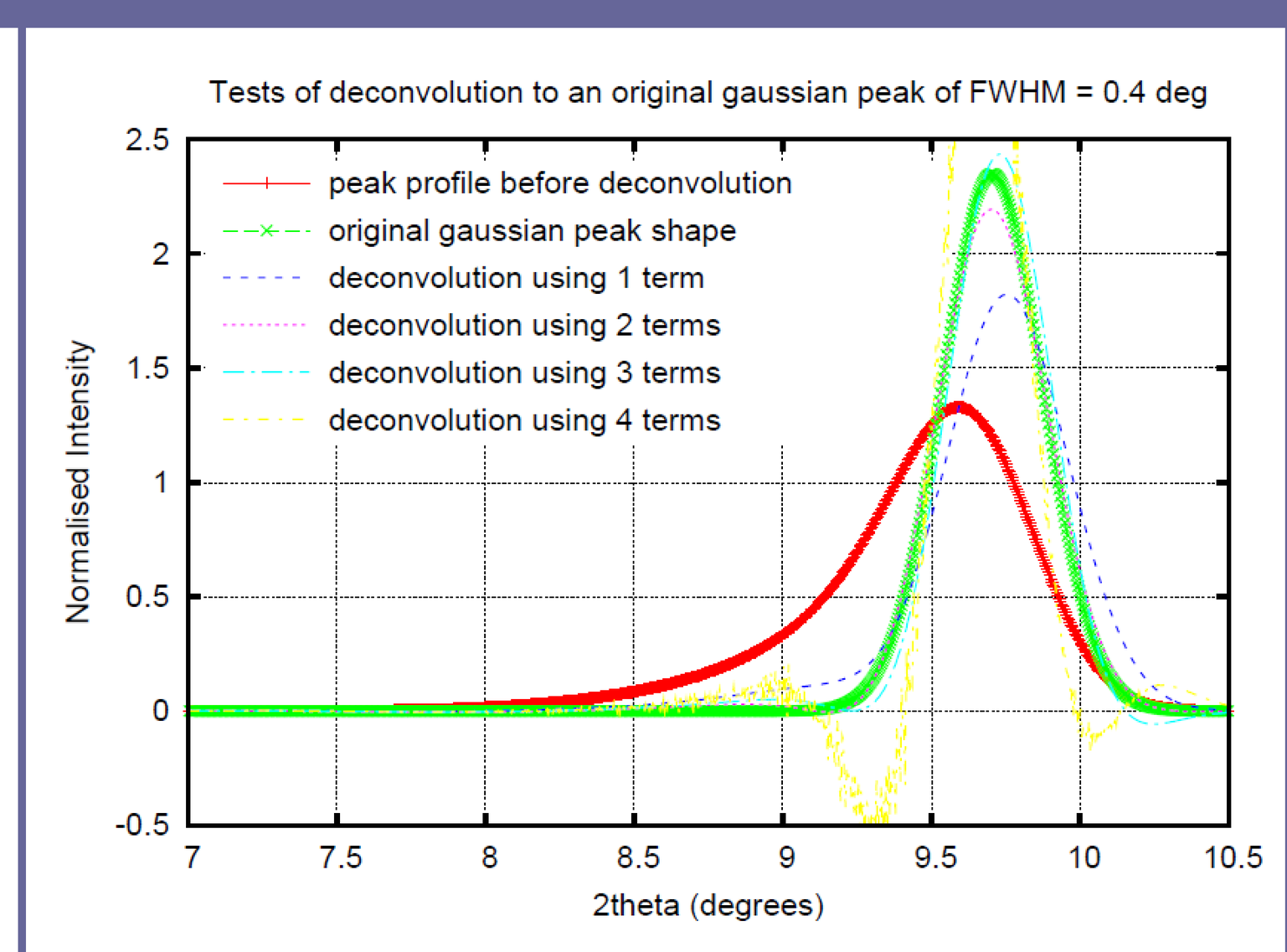


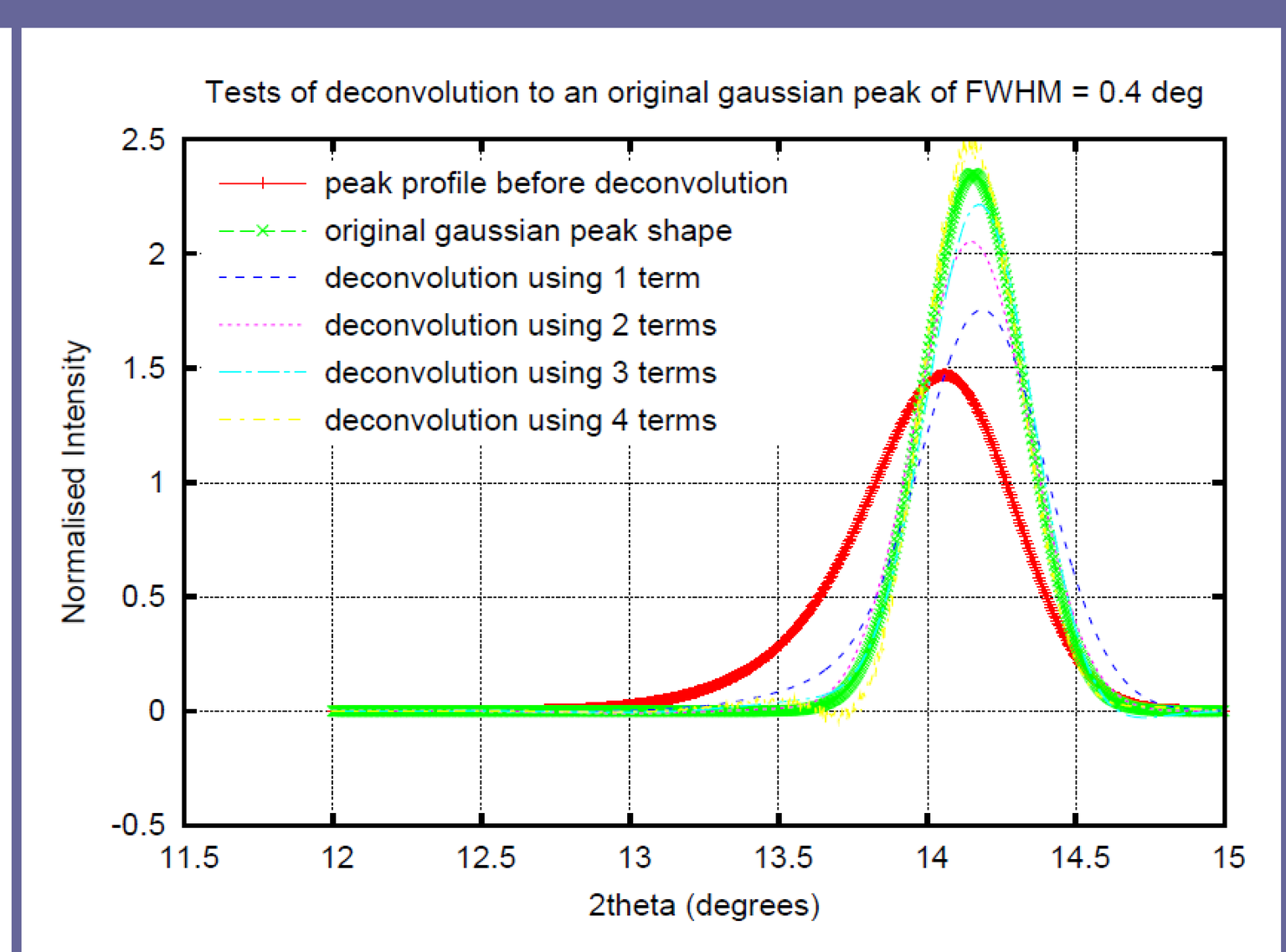




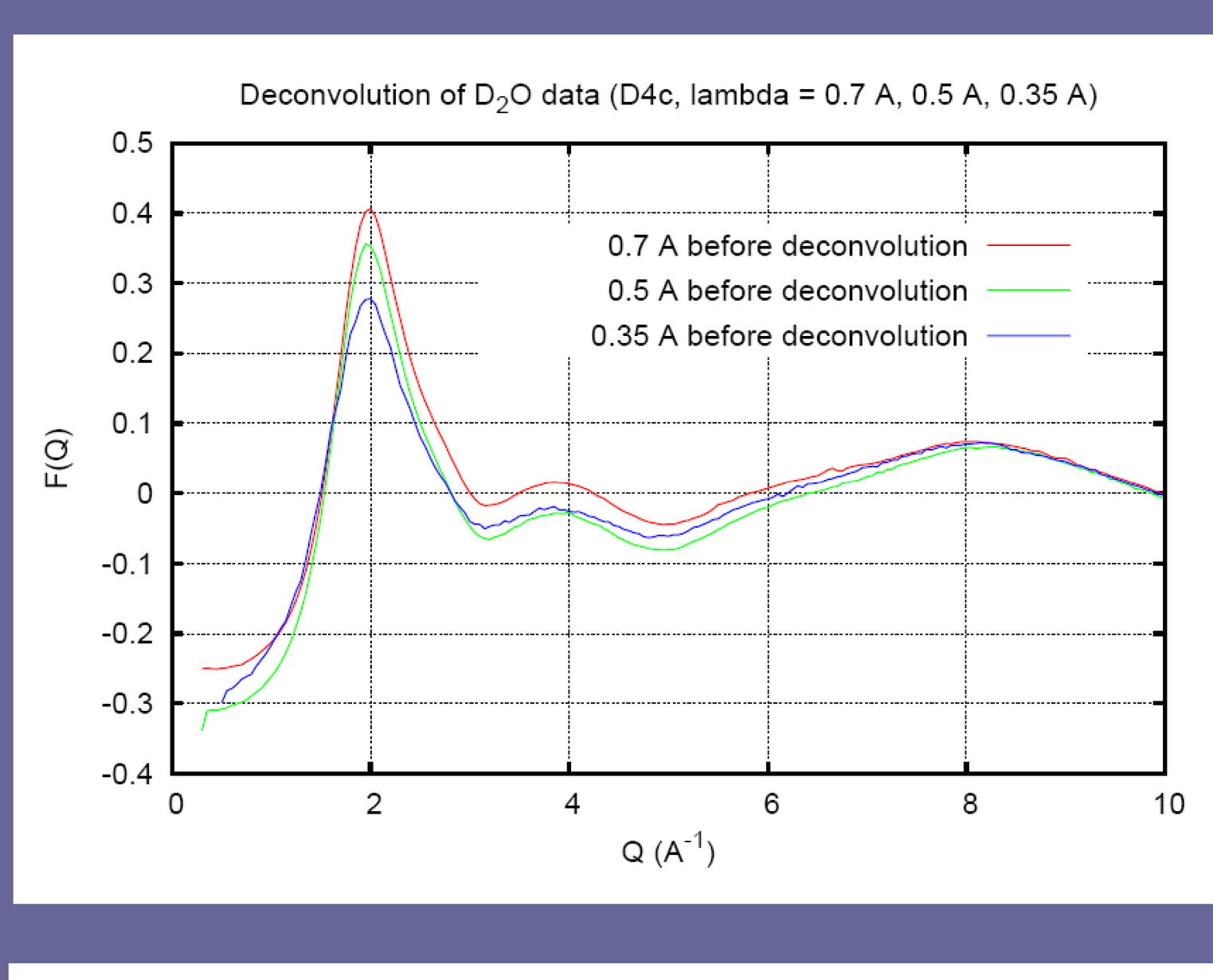
Gaussian tests: As a stringent test of our deconvolution algorithm, we convolved a Gaussian peak of FWHM = 0.4° by a typical D4c profile function at different 2θ angles and then used Decon to try to deconvolve the peaks back to the original Gaussian. At the lowest 2θ, the Taylor's expansion breaks down and the higher-order correction terms diverge (although the use of 2 correction terms remains quasi-stable). At the highest 2θ, more than 4 correction terms would be needed for complete convergence.

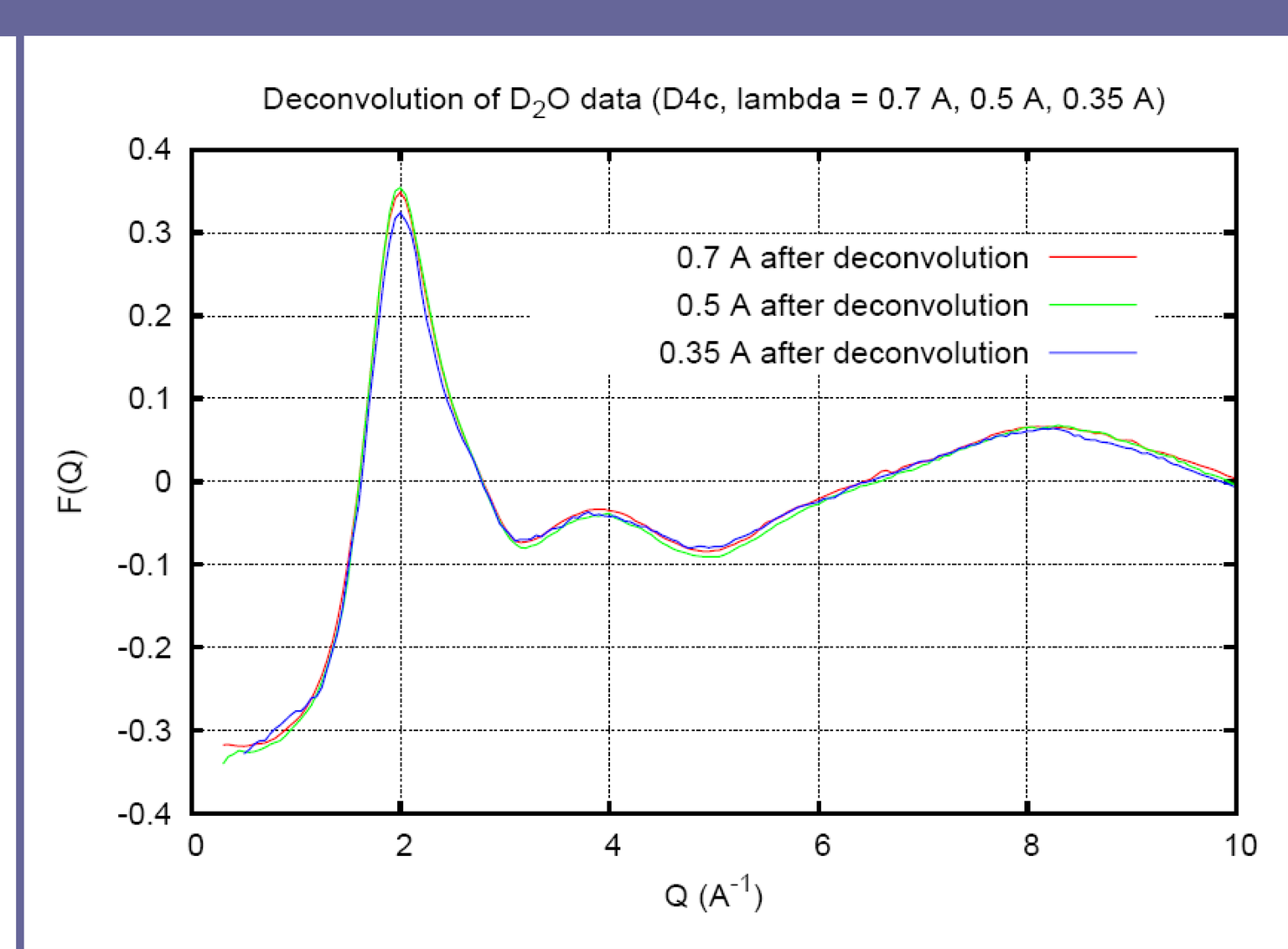


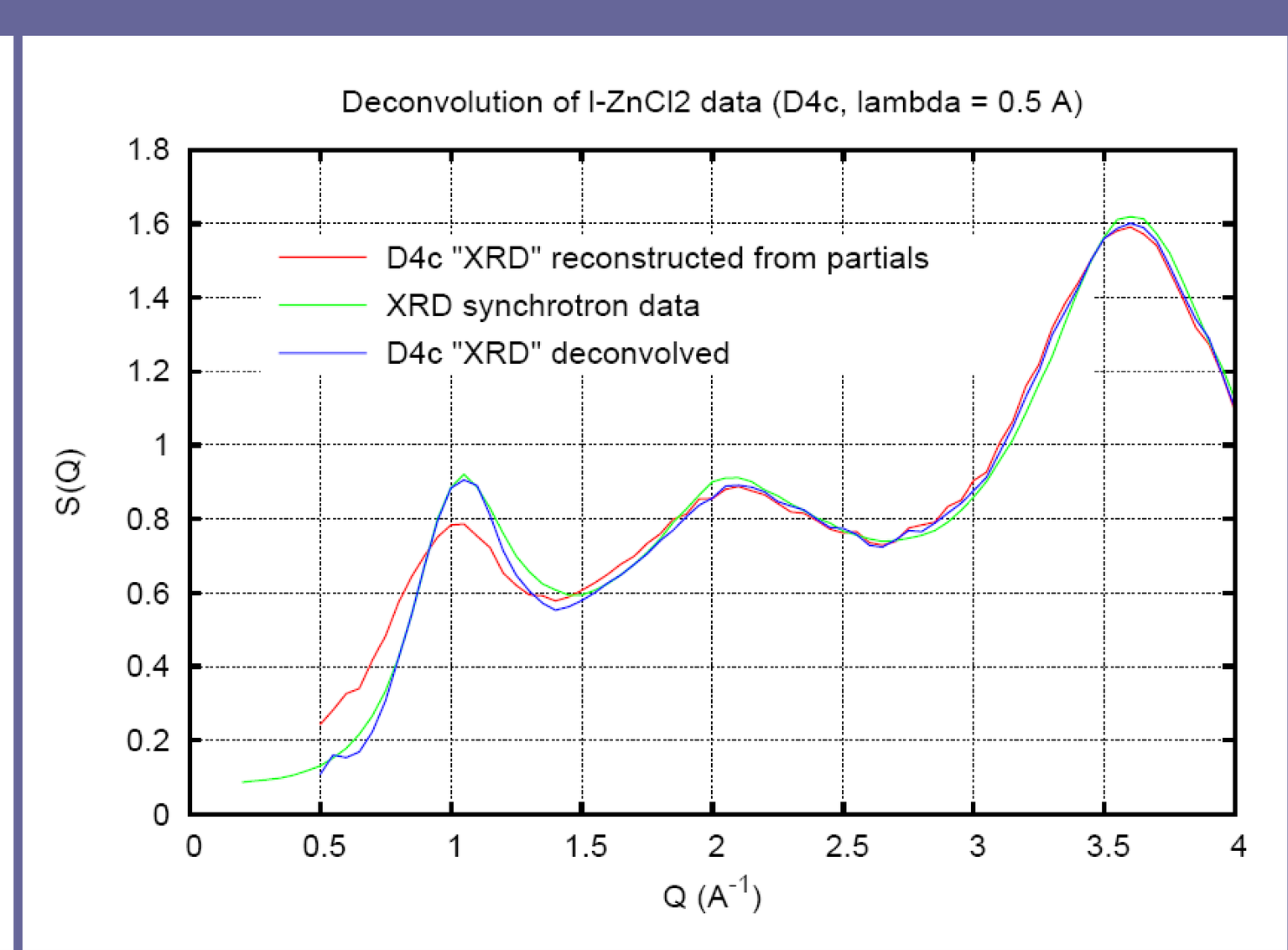




Applied to the structure factor of liquids/glasses: The main effect of the deconvolution procedure is to shift and sharpen the First Sharp Diffraction Peak (FSDP) where the resolution function is worst, especially at short wavelengths for a reactor-source diffractometer. The Decon results converge after 2 or 3 correction terms and not only agree for different wavelengths (D2O data), but also approach the high Q-space resolution that would be obtained from a synchrotron x-ray diffractometer (l-ZnCl2 data).







Applied to PDF analysis of powder diffraction data: Here the Bragg peaks are resolution-limited, thus offering an even harsher test of the deconvolution method. For this Ni powder data, we see that the Bragg peaks continue to be sharpened on applying all 4 Decon correction terms, although some noise becomes evident, and the final resolution is still less than that of spallation-source data, and certainly less than the theoretical limit of a δ-function.

Perhaps more interesting are the effects in r-space after Fourier transform of the powder diffraction pattern (i.e. PDF analysis). In the special case of a Gaussian resolution function [9] with the same FWHM of ΔQ at all $Q = (4\pi/\lambda) \cdot \sin(\theta)$, the PDF in r-space is modulated (i.e. multiplied) by a Gaussian centred at r = 0 and with a FWHM of about $\Delta r = 5.55 / \Delta Q$ corresponding to the neutron coherence volume size [10]. For D4c at λ= 0.5 Å, FWHM_Δr = 60 Å and thus at r = HWHM = 30 Å the intensity of the PDF already falls by a factor of 2. Application of 3 correction terms has the effect of "extending" the coherence volume: the D4c PDF then has an amplitude resembling the spallation-source PDF out to r ~ 30 Å.

[9] P.S. Salmon, *J. Phys. Condens. Matter* **18** (2006) 11443–11469.
[10] P. Chirawatkul, et al, *Phys. Rev. B* **83** (2011) 014203.