Size-Strain Analysis Assignment - Answers

Below I give the results that I obtained using the various techniques. You can compare my results and yours to the experts results that were obtained during the size-strain round robin sponsored by Davor Balzar at NIST and UC-Boulder. Unlike some other methods it is difficult to prepare standards for this type of analysis with size and strain distributions that can be independently verified by other techniques (methods like TEM and BET measurements are sensitive to particle size rather than crystallite size, and other methods of quantitatively measuring microstrain are not well known, to me anyway). However, the round robin gives us a reasonably good set of "correct answers" since this sample was analyzed using a variety of techniques, instrumental data collection procedures, and people and the results are reasonably consistent. In brief the results of the round robin analysis were as follows:

- The broadening is dominated by crystallite size broadening effects, and the microstrain contribution to the broadening appears to be negligible.
- The average volume weighted domain (crystallite) size is 226(9) Angstroms, while the average area (surface) weighted domain (crystallite) size is 168(21) Angstroms.
- The crystallite size distribution is fairly narrow, and the most common crystallite size falls at roughly 135 A.
- Since I have not corrected for instrumental broadening, my results should consistently give crystallite sizes that are smaller than the results obtained in the round robin.

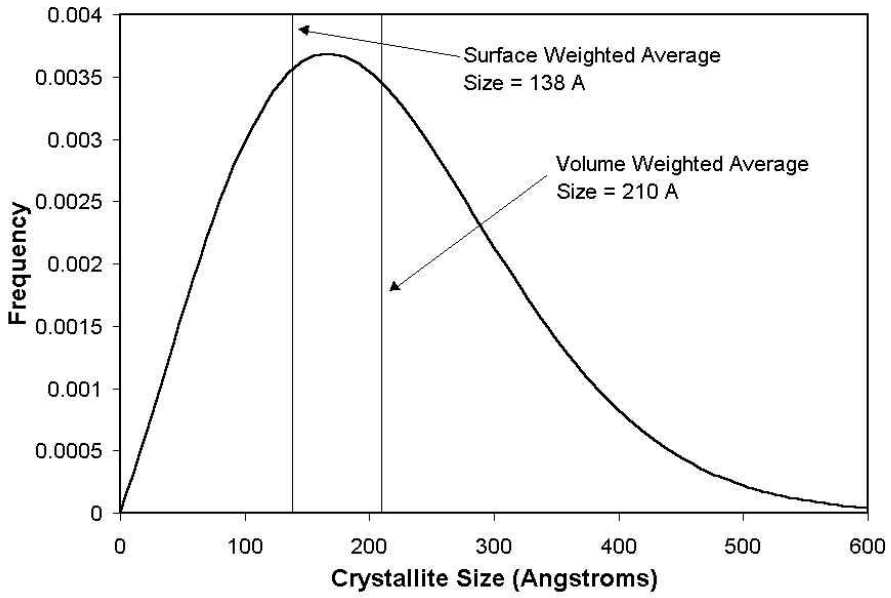
Keeping these things in mind I have obtained the following results:

3. Run Breadth and open the file Breadth.out.

(a) Record the values for the surface weighted and volume weighted average crystallite size.

- Average volume weighted domain size = 210(2) Angstroms
- Average surface weighted domain size = 138(2) Angstroms

(b) Plot the volume weighted crystallite size distribution (contained in the file disfunv.dat).

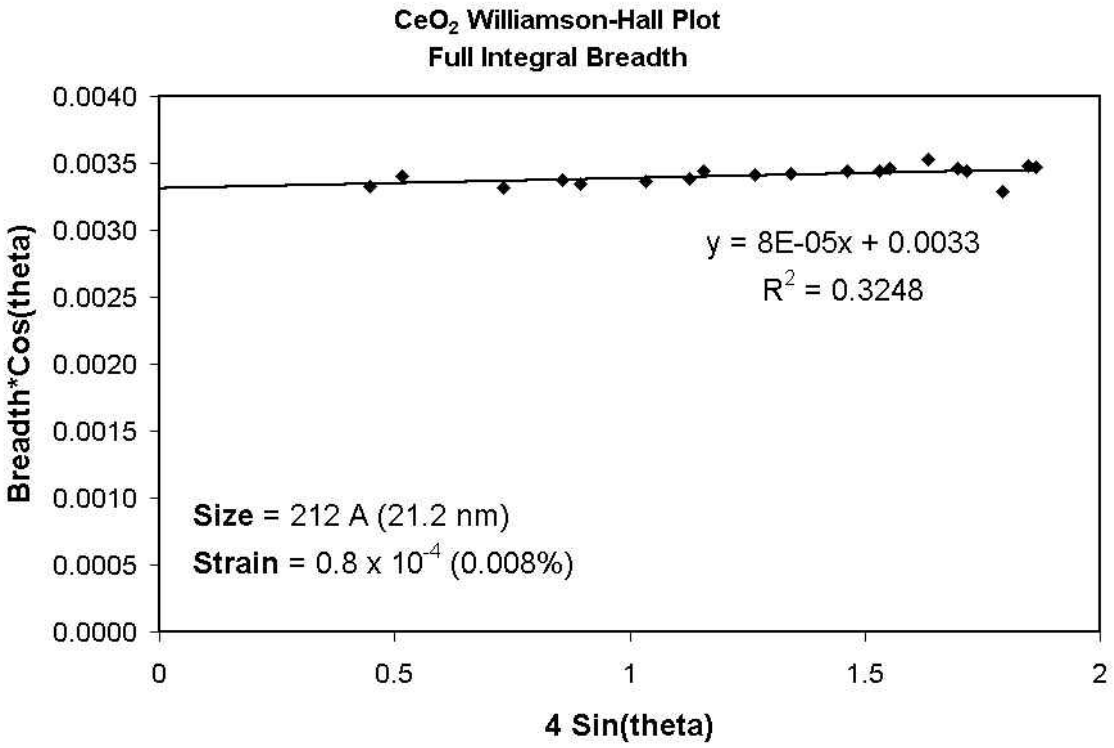


(c) Record the Size (D(A)) and Strain (eps) values recorded from the simplified integral breadth methods {keep in mind that the Cauchy function is another name for a Lorentzian function}.

- Cauchy(Size)-Cauchy(Strain) gives Average volume weighted crystallite size = 212 A, Strain = 0.8 x 10^{-4}
- Cauchy(Size)-Gauss(Strain) gives Average volume weighted crystallite size = 209 A, Strain = 3.2 x 10^{-4}
- Gauss(Lor)-Gauss(Strain) gives Average volume weighted crystallite size = 209 A, Strain = 4.7 x 10^{-4}

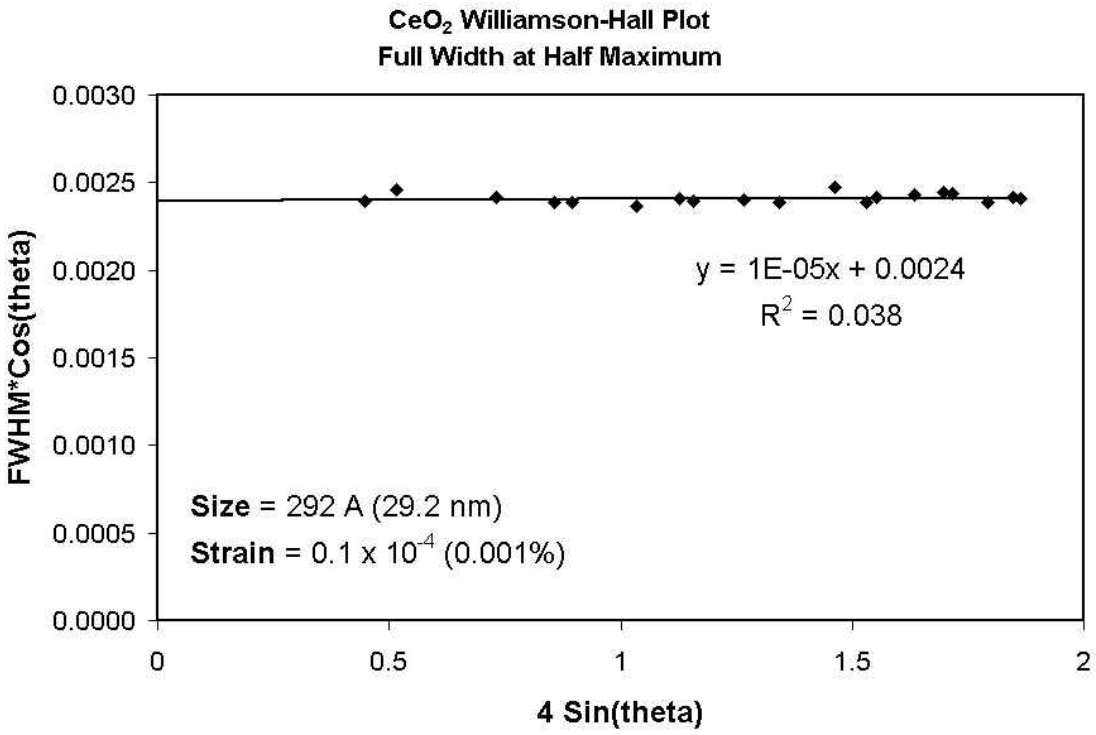
4. Take the integral breadths and 2-theta positions and construct a Williamson-Hall plot to determine average values for Volume weighted crystallite size and microstrain. The integral breadths are calculated by Breadth and tabulated in the breadth.out file.

This should correspond to the Cauchy-Cauchy result from simplified integral breadth methods given in the Breadth.out file. So it is good to see that my results were essentially the same: Average volume weighted crystallite size = 212 A, Strain = 0.8 x 10^{-4}



5. Construct a Williamson-Hall plot using FWHM values instead of integral breadths. How much difference does it make.

Since the FWHM is generally smaller than the Integral Breadth (certainly for Lorentzian peaks) one would expect that the average size will be larger, and that is indeed the result: Average volume weighted crystallite size = 292 A, Strain = 0.1 x 10^{-4}



7. Refine the data using a Rietveld program such as GSAS, and extract the crystallite size and strain parameters from the profile coefficients.

Using the Thompson-Cox-Hastings pseudo-voigt function that is employed by many Rietveld programs there are potentially four parameters associated with the Gaussian component of the peak (U, V, W & P) and two parameters associated with the Lorentzian component of the peak (X & Y). Of these six variables X is associated with the Lorentzian size broadening, Y with the Lorentzian strain broadening, P with the Gaussian size broadening and U with the Gaussian strain broadening, while V and W have no direct correlation with size and strain broadening. I thought it would be interesting to see how the results vary depending upon which profile coefficients I elected to use to fit the profile. The results are as follows:

a. Lorentzian size broadening only

- X = 10.70(5)
- Y = 0
- U = 0
- V = 0
- W = 0
- P = 0
- Rwp = 12.54%
- R(F2) = 5.05%
- Lorentzian Size = 238(1) Angstroms
- Gaussian Size = ---
- Lorentzian Strain = ---
- Gaussian Strain = ---

b. Size and Strain broadening, assume peak shape is purely Lorentzian

- X = 9.59(7)
- Y = 5.1(3)
- U = 0
- V = 0

- W = 0
- P = 0
- Rwp = 12.02%
- R(F2) = 5.25%
- Lorentzian Size = 266(2) Angstroms
- Gaussian Size = ---
- Lorentzian Strain = 0.2 x 10^{-4}
- Gaussian Strain = ---

d. Size broadening only, assume peak shape is mixed Lorentzian/Gaussian

- X = 7.90(3)
- Y = 0
- U = 0
- V = 0
- W = 0
- P = 14.0(2)
- Rwp = 7.39%
- R(F2) = 5.00%
- Lorentzian Size = 323(1) Angstroms
- Gaussian Size = 428(3) Angstroms
- Lorentzian Strain = ---
- Gaussian Strain = ---

e. Size and Strain broadening, assume peak shape is mixed Lorentzian/Gaussian

- X = 6.79(7)
- Y = 5.6(3)
- U = 0(3)
- V = 0
- W = 0
- P = 14.7(2)
- Rwp = 7.23%
- R(F2) = 4.97%
- Lorentzian Size = 376(4) Angstroms
- Gaussian Size = 417(3) Angstroms
- Lorentzian Strain = 0.2 x 10^{-4}
- Gaussian Strain = ---

f. Refine all profile parameters

- X = 6.73(7)
- Y = 5.9(3)
- U = 12(7)
- V = -19(4)
- W = 2.9(6)
- P = 14.0(2)
- Rwp = 7.01%
- R(F2) = 5.08%
- Lorentzian Size = 379(4) Angstroms
- Gaussian Size = 428(3) Angstroms

- Lorentzian Strain = 0.2 x 10^{-4}
- Gaussian Strain = 3.8 x 10^{-4}

As you can see there is considerable variation in the results depending upon which profile parameters I choose to refine, with (Lorentzian) crystallite size results varying from 238 A to 379 A. Some conclusions I draw from this analysis:

- The result which is in best agreement with the Integral Breadth and Double Voigt methods is to assume only Lorentzian size broadening. In this case we attribute all of the broadening to the size effect and treat the peaks as purely Lorentzian. Unfortunately, this approach gives the worst fit to the pattern, and so does not do a good job of accurately modeling the peak shapes.
- One can obtain a reasonably good fit to the pattern assuming only size broadening (refining only X and P). This is in agreement with the Williamson-Hall analysis. However, the peaks clearly have mixed Gaussian and Lorentzian character. This suggests that in general it might be useful to construct a Williamson-Hall plot prior to refinement in order to see which profile coefficients are needed (or at least should be refined first).
- If one is forced to refine both Lorentzian and Gaussian size broadening to accurately model the peak shape (as in this case), both the Lor. and Gaussian estimates of crystallite size are much too large. However, it is not immediately clear to me how to combine these results and get an accurate estimate of the crystallite size. (Though perhaps there may be a good way to do this). This effect was also apparently seen by others in the size-strain round robin since a value of ~360 Angstroms, with a fairly large error bar is reported for the Rietveld determination of crystallite size. In these cases it seems difficult to convert directly from the Rietveld profile coefficients to size and strain values.

Conclusions

The following points summarize my conclusions with this exercise, if one wants to obtain results which are meaningful in terms of their absolute accuracy. The restrictions are probably somewhat less stringent if you only seek results which show trends in a semi-quantitative manner. Also it should be noted that this sample was fairly easy to analyze for two reasons (a) there is essentially no strain broadening, and (b) the sample peak broadening is roughly 7 times larger than the instrumental peak broadening. More care must be taken when both size and strain are present, and when the magnitude of the sample and instrumental broadening become more equivalent.

- The Williamson-Hall method and the volume weighted crystallite size obtained from the double-voigt method are found to be in very good agreement with each other. Also in this case Breadth carried out the Williamson-Hall analysis very accurately (under simplified integral breadth methods) and there was no reason to repeat the analysis manually using a spreadsheet. However, visual inspection of the Williamson-Hall plot is probably a good idea in order to see how reliable the results are.
- It is difficult to extract accurate parameters from Rietveld analysis when the peak shape is mixed Gaussian-Lorentzian. In this case the accuracy was improved somewhat by sacrificing goodness of fit in favor of a simplified peak shape (Lorentzian size broadening only).
- Using FWHMs instead of Integral Breadths to describe the peak width leads to a considerable overestimation of the crystallite size, in this instance the estimate changes from 212 A to 292 A.
- In this instance not correcting for instrumental broadening led a decrease of 14 Angstroms in the volume weighted average crystallite size (226 A to 212 A), and 30 Angstroms in the surface (area) weighted crystallite size (168 A to 138 A). These effects will become much more extreme as the sample broadening becomes more comparable to the instrumental broadening.