Supplementary material to the manuscript "The real background and peak asymmetry in diffraction on nanocrystalline metals"

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1 Solution of inequality requiring column length distribution to be positive

The column length distribution is proportional to the second derivative of A(L) :

$$\frac{d^2A(L)}{dL^2} = [(2\pi L\beta_G^2 + 2\beta_C)^2 - 2\pi\beta_G^2]A(L) \quad (1)$$

The requirement of positivity is :

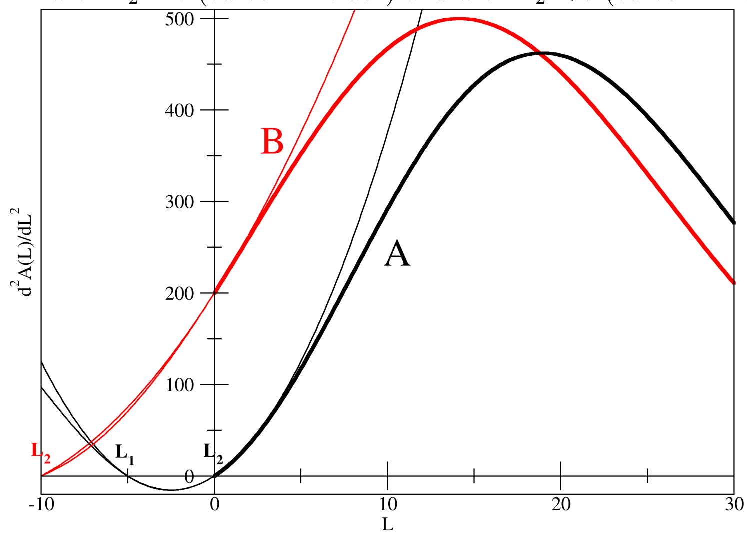
$$(2\pi L\beta_G^2 + 2\beta_C)^2 \geq 2\pi\beta_G^2 \quad (2)$$

The function $F(L) = 4\pi^2L^2\beta_G^4 + 8\pi L\beta_G^2\beta_C + 4\beta_C^2 - 2\pi\beta_G^2$ is quadratic versus L with two roots

$$L_1 = -\frac{\beta_C}{\pi\beta_G^2} - \frac{1}{\sqrt{2\pi}\beta_G}, L_2 = -\frac{\beta_C}{\pi\beta_G^2} + \frac{1}{\sqrt{2\pi}\beta_G} \quad (3)$$

A graphical representation of F(L) is a parabola with two arms diverging to $+\infty$. The above inequality (2) is thus fulfilled for all positive L (describing length of column of atoms) only when $L_2 \leq 0$. Otherwise for some positive L the parabola turns negative and so the column length frequency.
The condition $L_2 \leq 0$ is equivalent to the requirement $\beta_C \geq \sqrt{\frac{\pi}{2}}\beta_G$.
The equality corresponds to the approximate shape of the column length distribution shown in Suppl-fig.1, curve A (black- $L_2 = 0$). The strict inequality results in a column length distribution similar to the presented as curve B (red- $L_2 < 0$). The case when $L_2 > 0$ always leads to negative values of F(L) (and CLD) within physically interpretable range of $L > 0$. A sum of CLDs from cubooctahedral shape for 200 and 220 reflections, as shown in fig.2, always results in CLD(0)=0 and corresponds to the case $L_2 = 0$. On the other hand analysis of 111 reflection shape assuming cubooctahedral crystallites distribution (fig.2) has to assume $CLD(0) > 0$ and corresponds to the case $L_2 < 0$. In this case one has to fit 111 profile with Voigt functions having $\beta_C > \sqrt{\frac{\pi}{2}}\beta_G$ and the ratio of β_C/β_G can approach 1.7 - 2.

Figure 1: Calculated Column Length Distribution for the model described by equation 1 with $L_2 = 0$ (curve A - black) and with $L_2 < 0$ (curve B - red).



2 Preparation of 20%Au/C sample

The following reagents and materials were used during the synthesis process: carbon Vulcan XC 72 (Cabot Corporation), hydrogen tetrachloroaurate(III) trihydrate ($HAuCl_4 * 3H_2O$, $99,9\%$, $AlfaAesar$), sodium borohydride ($NaBH_4$, 99%, $Sigma{-}Aldrich$), trisodium citrate dihydrate ($Na_3C_6H_5O_7, ppa, Chempur$), propan-2-ol (ppa, Stanlab) and double-distilled water.
In order to prepare 500 mg of the catalyst, 400 mg of carbon was suspended (ultrasonication aided by mechanical stirring) in 85 ml mixture of propan-2-ol and water (volume ratio 3:1). 20 ml of 0,82%wt (0,03512 M) tetrachloroaurate solution was diluted under vigorous stirring at room temperature with 1725 ml of water and 17 ml of 4%wt trisodium citrate solution was added. In a separate beaker a reducing agent solution was prepared. It consisted of sodium borohydride (15 mg) dissolved in 4%wt aqueous trisodium citrate (17 ml). Addition of the reducing agent solution to citrate-protected aqueous tetrachloroaurate resulted in immediate color change to deep red. Following 5 minutes the carbon suspension was purged into the red gold colloid. Such a mixture was stirred for 48h in darkness, then it was filtered and rinsed with water until no chloride anions were detected. Finally, the catalyst was dried under vacuum overnight in temperatures not exceeding $40°C$. A ready-for-use catalyst was stored in darkness in a desiccator.

3 The best fit Voigt functions parameters for 20%Au/C sample 220 peak from Fityk program

The sample exposed to He:

PeakType	Center	Height	Area	FWHM	β_G	β_C/β_G.
Voigt	0.5419(1)	1337(50)	55.4(1)	0.0289(2)	0.00855(4)	1.26.
Voigt	0.53931(2)	5288(50)	90.2(2)	0.01191(1)	0.003518(4)	1.26.

The sample exposed to O_2:

PeakType	Center	Height	Area	FWHM	β_G	β_C/β_G.
Voigt	0.539204(4)	4580(20)	74.5(5)	0.01137(2)	0.003359(6)	1.26.
Voigt	0.54117(1)	1615(18)	56.2(4)	0.0243(2)	0.00717(5)	1.26.

The sample exposed to H_2:

PeakType	Center	Height	Area	FWHM	β_G	β_C/β_G.
Voigt	0.542327(1)	822(9)	34.1(3)	0.028946(1)	0.00855416(1)	1.26.
Voigt	0.538972(4)	982(20)	9.5(2)	0.00679(5)	0.00201(2)	1.26.
Voigt	0.539416(6)	4453(12)	87.942(3)	0.01379(4)	0.004075(11)	1.26.

The peak position is in $sin(\theta)$ scale. The figures in parentheses are measure of error of the last significant figure. The error estimation is a difficult task also because some peak parameters are correlated. The estimation of least square errors requires calculation of the full Hessian matrix close to the minimum. It represents then variance/covariance matrix of the parameters enabling errors estimate but the used program Fityk does not provide finite difference approximation of the Hessian. The additional fit parameter introduced here was the background scaling constant. The best fit has been optimized against this constant and some feeling of the errors has been given above via shift of the best fit values when the background is changed by about 10^{-4} of the peak value at the maximum. This was an approximate value of the step in the background level that was used when arriving on the best fit.
The above considerations concern only statistical error of the nonlinear fit routine. As is usually the case the systematic errors are not possible to evaluate and are here mostly due to asumptions determining shape of the peak background line.