JOURNAL OF
SYNCHROTRON
RADIATION

Volume 28 (2021)

Supporting information for article:

A refraction correction for buried interfaces applied to *in situ* grazing incidence X-ray diffraction studies on Pd electrodes

Alan Landers, David M. Koshy, Soo Hong Lee, Walter S. Drisdell, Ryan C. Davis, Christopher Hahn, Apurva Mehta and Thomas F. Jaramillo

Full derivation of refraction correction

General expression for refraction

n refers to the refractive index. δ and β refer to the real and imaginary components of the refractive index. Subscripts of 1 and 2 refer to the liquid and solid portions of the interface respectively.

In this portion of the derivation, the angle θ could represent either the angle α or the angle γ

Snell's Law

$$n_1 \cos(\theta_1) = n_2 \cos(\theta_2)$$

$$\cos(\theta_2) = \frac{n_1}{n_2}\cos(\theta_1)$$

Double angle identity and small angle approximation

$$1 - \frac{\theta_2^2}{2} = \frac{n_1}{n_2}(1 - \frac{\theta_1^2}{2})$$

$$2 - \theta_2^2 = \frac{2 * n_1}{n_2}(1 - \frac{\theta_1^2}{2})$$

$$\theta_2^2 = 2 - \frac{2 * n_1}{n_2}(1 - \frac{\theta_1^2}{2})$$

$$\theta_2 = \sqrt{2 - \frac{2 * n_1}{n_2}(1 - \frac{\theta_1^2}{2})}$$

$$\theta_2 = \sqrt{2 - \frac{2 * n_1}{n_2} + \frac{n_1 * \theta_1^2}{n_2}}$$

Define n_{eff}

$$n_{eff} = \frac{n_2}{n_1}$$

$$n_{eff} = \frac{1 - \delta_2 - i\beta_2}{1 - \delta_1 - i\beta_1}$$

$$n_{eff} = \frac{1 - \delta_2 - i\beta_2}{1 - \delta_1 - i\beta_1} * \frac{1 + \delta_1 + i\beta_1}{1 + \delta_1 + i\beta_1}$$

$$n_{eff} = \frac{1 - \delta_2 - i\beta_2 + \delta_1 - \delta_1\delta_2 - i\delta_1\beta_2 + i\beta_1 - i\delta_2\beta_1 - i^2\beta_1\beta_2}{1 - \delta_1 - i\beta_1 + \delta_1 - {\delta_1}^2 - i\beta_1\delta_1 + i\beta_1 - i\delta_1\beta_1 - i^2\beta_1^2}$$

$$n_{eff} = \frac{1 - \delta_2 - i\beta_2 + \delta_1 - \delta_1\delta_2 - i\delta_1\beta_2 + i\beta_1 - i\delta_2\beta_1 + \beta_1\beta_2}{1 - {\delta_1}^2 - i\beta_1\delta_1 - i\delta_1\beta_1 + \beta_1^2}$$

$$n_{eff} = \frac{1 - \delta_2 + \delta_1 - i\beta_2 + i\beta_1 - \delta_1\delta_2 - i\delta_1\beta_2 - i\delta_2\beta_1 + \beta_1\beta_2}{1 - {\delta_1}^2 + \beta_1^2 - 2i\delta_1\beta_1}$$

Because δ_1, β_1 << 1 in the X-ray energy range, the denominator can be simplified to 1

$$n_{eff} = 1 - \delta_2 + \delta_1 - i\beta_2 + i\beta_1 - \delta_1\delta_2 - i\delta_1\beta_2 - i\delta_2\beta_1 + \beta_1\beta_2$$

$$n_{eff} = 1 - (\delta_2 - \delta_1) - i(\beta_2 - \beta_1) - \delta_1\delta_2 + \beta_1\beta_2 - i\delta_1\beta_2 - i\delta_2\beta_1$$

Because δ_1, β_1 << 1 in the X-ray energy range, $\delta_1\delta_2$, $\beta_1\beta_2$, $\delta_1\beta_2$, $\delta_2\beta_1$ << $(\delta_2 - \delta_1) - i(\beta_2 - \beta_1)$. We also assume that the materials have sufficiently different optical constants to result in observable refraction

$$n_{eff} = 1 - (\delta_2 - \delta_1) - i(\beta_2 - \beta_1)$$

Define $\delta_{eff} = \delta_2 - \delta_1$ and $\beta_{eff} = \beta_2 - \beta_1$

$$n_{eff} = \frac{n_2}{n_1} = 1 - \delta_{eff} - i\beta_{eff}$$

Substitute expression for n_{eff} into expression for refraction derived above

$$\theta_2 = \sqrt{2 - \frac{2}{n_{eff}} + \frac{\theta_1^2}{n_{eff}}}$$

$$\theta_2 = \sqrt{\frac{2n_{eff} - 2 + \theta_1^2}{n_{eff}}}$$

$$\theta_2 = \sqrt{\frac{2(1 - \delta_{eff} - i\beta_{eff}) - 2 + \theta_1^2}{1 - \delta_{eff} - i\beta_{eff}}}$$

$$\theta_2 = \sqrt{\frac{2 - 2\delta_{eff} - 2i\beta_{eff} - 2 + \theta_1^2}{1 - \delta_{eff} - i\beta_{eff}}}$$

$$\theta_2 = \sqrt{\frac{-2\delta_{eff} - 2i\beta_{eff} + \theta_1^2}{1 - \delta_{eff} - i\beta_{eff}}}$$

$$\theta_2 = \sqrt{\frac{\theta_1^2 - 2\delta_{eff} - 2i\beta_{eff}}{1 - \delta_{eff} - i\beta_{eff}} * \frac{1 + \delta_{eff} + i\beta_{eff}}{1 + \delta_{eff} + i\beta_{eff}}}$$

$$\theta_2 = \sqrt{\frac{\theta_1^2 - 2\delta_{eff} - 2i\beta_{eff} + \delta_{eff}(\theta_1^2 - 2\delta_{eff} - 2i\beta_{eff}) + i\beta_{eff}(\theta_1^2 - 2\delta_{eff} - 2i\beta_{eff})}{1 - \delta_{eff} - i\beta_{eff} + \delta_{eff}(1 - \delta_{eff} - i\beta_{eff}) + i\beta_{eff}(1 - \delta_{eff} - i\beta_{eff})}}$$

$$\theta_2 = \sqrt{\frac{\theta_1^2 - 2\delta_{eff} - 2i\beta_{eff} + \delta_{eff}\theta_1^2 - 2{\delta_{eff}}^2 - 2i\beta_{eff}\delta_{eff} + i\beta_{eff}\theta_1^2 - 2i\delta_{eff}\beta_{eff} - 2i^2{\beta_{eff}}^2}{1 - \delta_{eff} - i\beta_{eff} + \delta_{eff} - {\delta_{eff}}^2 - i\delta_{eff}\beta_{eff} + i\beta_{eff} - i\delta_{eff}\beta_{eff} - i^2{\beta_{eff}}^2}}$$

$$\theta_2 = \sqrt{\frac{\theta_1^2 - 2\delta_{eff} + \delta_{eff}\theta_1^2 - 2i\beta_{eff} + i\beta_{eff}\theta_1^2 + 2\beta_{eff}{}^2 - 2\delta_{eff}{}^2 - 4i\delta_{eff}\beta_{eff}}{1 - \delta_{eff}{}^2 + \beta_{eff}{}^2 - 2i\delta_{eff}\beta_{eff}}}$$

Since δ_{eff} and β_{eff} are small,

$1 >> - \delta_{eff}^2 + \beta_{eff}^2 - 2i\delta_{eff}\beta_{eff}$

$\theta_1^2 - 2\delta_{eff} + \delta_{eff}\,\theta_1^2 - 2i\beta_{eff} + i\beta_{eff}\,\theta_1^2 >> 2\,\beta_{eff}^2 - 2\delta_{eff}^2 - 4i\delta_{eff}\beta_{eff}$

$$\theta_2 = \sqrt{\theta_1^2 - 2\delta_{eff} + \delta_{eff}\theta_1^2 - 2i\beta_{eff} + i\beta_{eff}\theta_1^2}$$

$$\theta_2 = \sqrt{(\theta_1^2 - 2\delta_{eff} + \delta_{eff}\theta_1^2) + i(\beta_{eff}\theta_1^2 - 2\beta_{eff})}$$

Electric Field Vector Inside Solid, (x,z) are x and z components of field

$$k' = k * n_2 * (x, z)$$

$$k' = k * n_2 * (cos(\theta_2), sin(\theta_2))$$

Direction of Refracted X-rays

$$\frac{(k_r')_z}{(k_r')_x} = Re[\frac{k * n_2 * sin(\theta_2)}{k * n_2 * cos(\theta_2)}]$$

$$\frac{(k_r')_z}{(k_r')_x} = Re[tan(\theta_2)]$$

Small angle approximation

$$\frac{(k_r')_z}{(k_r')_x} = Re[\theta_2]$$

Substituting from above

$$\frac{(k_r')_z}{(k_r')_x} = Re[\sqrt{(\theta_1^2 - 2\delta_{eff} + \delta_{eff}\theta_1^2) + i(\beta_{eff}\theta_1^2 - 2\beta_{eff})}]$$

General formula for the square root of a complex number

$$\sqrt{a + bi} = \pm(c + di)$$

$$c = \sqrt{\frac{a + \sqrt{a^2 + b^2}}{2}}$$

$$d = sgn(b)\sqrt{\frac{-a + \sqrt{a^2 + b^2}}{2}}$$

$$Re\left[\sqrt{a+bi}\right] = Re[\pm(c+di)] = \pm c = \pm\sqrt{\frac{a+\sqrt{a^2+b^2}}{2}}$$

Taking only the positive root

$$Re\left[\sqrt{a+bi}\right] = \sqrt{\frac{a+\sqrt{a^2+b^2}}{2}}$$

Applying the above formula

$$\frac{(k_r')_z}{(k_r')_x} = Re[\sqrt{(\theta_1^2 - 2\delta_{eff} + \theta_1^2\delta_{eff}) + i(-2\beta_{eff} + \theta_1^2\beta_{eff})}$$

$$= \sqrt{\frac{\theta_1^2 - 2\delta_{eff} + \theta_1^2\delta_{eff} + \sqrt{\left(\theta_1^2 - 2\delta_{eff} + \theta_1^2\delta_{eff}\right)^2 + (-2\beta_{eff} + \theta_1^2\beta_{eff})^2}}{2}}$$

$$\frac{(k_r')_z}{(k_r')_x} = \frac{1}{\sqrt{2}}\sqrt{\theta_1^2 - 2\delta_{eff} + \theta_1^2\delta_{eff} + \sqrt{\left(\theta_1^2 - 2\delta_{eff} + \theta_1^2\delta_{eff}\right)^2 + (-2\beta_{eff} + \theta_1^2\beta_{eff})^2}}$$

$$\frac{(k_r')_z}{(k_r')_x} = \frac{1}{\sqrt{2}}\sqrt{\sqrt{\left(\theta_1^2 - 2\delta_{eff} + \theta_1^2\delta_{eff}\right)^2 + (-2\beta_{eff} + \theta_1^2\beta_{eff})^2} - 2\delta_{eff} + \theta_1^2\delta_{eff} + \theta_1^2}$$

Derive critical angle

Snell's law

$$n_1\cos(\theta_1) = n_2\cos(\theta_2)$$

At the critical angle θ_2=0

$$n_1\cos\left(\theta_{c,eff}\right) = n_2\cos(0)$$

$$\cos\left(\theta_{c,eff}\right) = \frac{n_2}{n_1}$$

Double angle identity ($\cos(2x)=1-2\sin^2(x)$)

$$1 - 2\left(sin\left(\frac{\theta_{c,eff}}{2}\right)\right)^2 = \frac{n_2}{n_1}$$

Small angle approximation ($\sin(x)\approx x$)

$$1 - \frac{\theta_{c,eff}^2}{2} = \frac{n_2}{n_1}$$

$$\theta_{c,eff}^2 = 2 - \frac{2n_2}{n_1}$$

Expressing critical angle in terms of n_{eff}, δ_{eff}, and β_{eff}

$$\theta_{c,eff}^2 = 2 - 2n_{eff} = 2 - 2(1 - \delta_{eff} - i\beta_{eff})$$

$$\theta_{c,eff}^2 = 2\delta_{eff} + 2i\beta_{eff}$$

Neglecting the imaginary portion because $\beta_{eff} < \delta_{eff}$

$$\theta_{c,eff}^2 = 2\delta_{eff}$$

Substituting the critical angle into the equation above

$$\frac{(k_r')_z}{(k_r')_x} = \frac{1}{\sqrt{2}}\sqrt{\sqrt{\left(\theta_1^2 - \theta_{c,eff}^2 + \frac{\theta_1^2\theta_{c,eff}^2}{2}\right)^2 + (-2\beta_{eff} + \theta_1^2\beta_{eff})^2} - \theta_{c,eff}^2 + \frac{\theta_1^2\theta_{c,eff}^2}{2} + \theta_1^2}$$

Value of correction

$$\Delta 2\theta = 2\theta_{apparent} - 2\theta_B$$

$$\Delta 2\theta = (\alpha_{app} + \gamma_{app}) - (\alpha_B + \gamma_B)$$

$$\Delta 2\theta = \left(\alpha_{app} - \alpha_B\right) + (\gamma_{app} - \gamma_B)$$

$$\begin{aligned}\Delta 2\theta &= \alpha_{app} \\ &- \frac{1}{\sqrt{2}}\sqrt{\sqrt{\left(\alpha_{app}^2 - \theta_{c,eff}^2 + \frac{\alpha_{app}^2\theta_{c,eff}^2}{2}\right)^2 + \left(-2\beta_{eff} + \alpha_{app}^2\beta_{eff}\right)^2} - \theta_{c,eff}^2 + \frac{\alpha_{app}^2\theta_{c,eff}^2}{2} + \alpha_{app}^2} \\ &+ \gamma_{app} \\ &- \frac{1}{\sqrt{2}}\sqrt{\sqrt{\left(\gamma_{app}^2 - \theta_{c,eff}^2 + \frac{\gamma_{app}^2\theta_{c,eff}^2}{2}\right)^2 + \left(-2\beta_{eff} + \gamma_{app}^2\beta_{eff}\right)^2} - \theta_{c,eff}^2 + \frac{\gamma_{app}^2\theta_{c,eff}^2}{2} + \gamma_{app}^2}\end{aligned}$$