

The Significance of Refractive Index “K” Values of 45 to 200 Å 2d LSMs, or, Why Your Long Wavelength Peak Markers May Not Line Up Correctly

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Most electron microprobes today contain at least one layered synthetic material (LSM) diffractor, with 2d values ranging from 45 to 200 Å, for acquisition of F to Be $K\alpha$. One of the touted features of these “pseudo-crystals” is the suppression of higher order diffractions, however in practice 2nd and 3rd order peaks can be observed. Pulse height discrimination is one option; however, it is impossible to totally remove all 2nd order peak counts with this method.

In situations where the element of interest is present at trace levels and the interfering element is a major element (e.g. F $K\alpha$ and 3rd order P $K\alpha$), it is incumbent upon the operator to verify that the interfering peak is removed by running detailed wavescans. The difficulty, however, can be in properly displaying/identifying the peak positions. Discrepancies were noted in the display, even the relative position, of these 2 closely spaced peaks using 2 different software packages. Following discussion with Stephen Reed (2001), the significance of the refractive index term K in the expanded form of Braggs Law became apparent, further clarified by reading M. Siegbahn’s 1925 treatise [1], in which he delved into “the invalidity of the Bragg interference equation in measurements of greater precision”. He derived a more exact equation that reduces to a correction of the 2d by $(1-k/n^2)$ [2]. Note that the MAXIMUM deviation (correction) is for $n=1$. This is somewhat counterintuitive, as one would think that the 2d could be simply backed out of measuring a known x-ray line (e.g. O $K\alpha$) and the sin theta of the peak center (and in fact this is what one manufacturer told me in 2004 as how they found 2d, and that they did not determine K).

In 2003, I carried out an informal poll of 14 other Cameca probes (SX50 and 100) of values they used for their 45, 60, 100 and 200 Å LSMs (PC0, 1, 2, 3), all presumably from the same manufacturer. The results are in Table 1, and show a wide range of 2d values. (I then found that Stephen Reed had found similar values when he did a similar survey 4 years before.) Why the wide variation? Some possibilities are: actual differences, or possibly errors in the determinations by someone at some step. Regardless, for EPMA analyses with peaking on actual elemental peaks (e.g. O $K\alpha$), it is not critical to have the 2d accurately determined, as EPMA is a relative procedure.

However, when interferences occur at positions in the vicinity of such peaks, the importance of having proper “crystal” settings, particular the K or refractive factor, is more critical, as the correction effectively goes to zero at high (e.g. $n=3$ or 4) values, but is greatest when $n=1$. For 45 Å LSM, the probe labs surveyed used K ranging from .001 to .01, for 60 Å, .00001 to .019, for 100 Å, .000058 to .04, and for 200 Å, .0001 to .01. Many of the K values likely lead to errors in the placement of markers on scans for lines interfering with Be, B, C, N, O and F $K\alpha$. The biggest error will be for the 1st order element peaks as they require the largest correction $(1-K)$ whereas a second order interference would be smaller $(1-K/4)$. *In the field determination of 2ds without consideration of the K factor will yield erroneous 2d calculations.* Proper determination of 2d and K is an iterative

process, with appropriate choices of materials combining the first order peak together with higher order ones (e.g. carbon coated MgO). Figure 1 shows scans on MgO, with O K α centered (not shown, to the left) and on the same scan, the error in position of n=2 O K α , n=4 Mg K α and offset of C K α from peak center, on the 98.5 Å LSM; following correction of the 2d and K, the markers correctly align (Figure 2), making peak identification on LSM much more straight forward.

References

- [1] M. Siegbahn, The Spectroscopy of X-Rays, Oxford, 1925, pp. 21-29.
- [2] S. Reed, Electron Microprobe Analysis, 2nd Edition, Cambridge, 1993, pp. 63-64

Figure 1

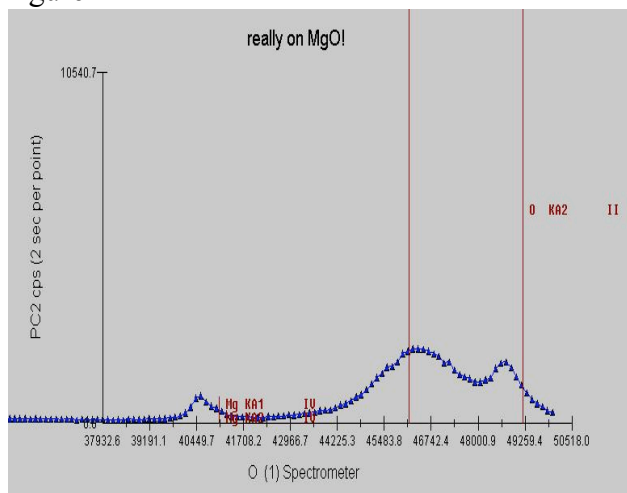


Figure 2

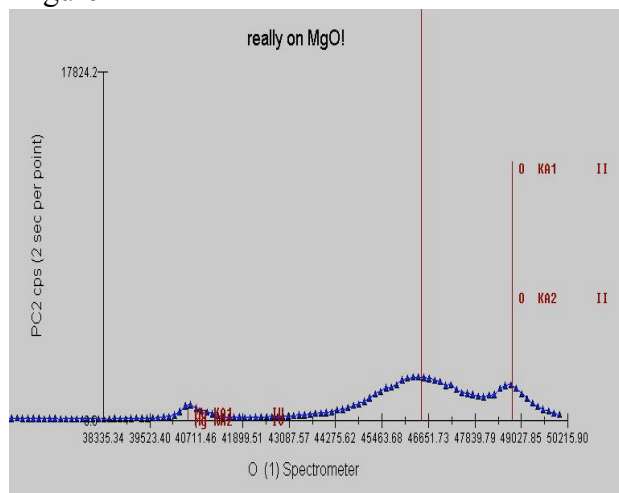


Fig 1-2: Red markers, left to right: 4th order Mg K α , C K α (n=1, from coat), and 2nd order O k α .

| TABLE 1 | PC0 | | PC1 | | PC2 | | PC3 | |
|-------------|-----------|----------|-----------|-------------|------------|---------------|-------------|------------|
| nominal 2d | 45 Å | | 60 Å | | 100 Å | | 200 Å | |
| Lab | 2d | K | 2d | K | 2d | K | 2d | K |
| 1 (UW-old) | 45.0 | 0.01483 | 61.0 | 0.010 | 95.2 | 0.013 | 200.0 | 0.01 |
| 2 | | | 62.5 | 0.00001 | 95.0 | 0.00216 | 198.2 | 0.0001 |
| 3 | | | 59.8 | 0.01483 | 94.9 | 0.0216 | | |
| 4 | | 0.00905 | | 0.01315 | | 0.03777 | | 0.04146 |
| 5 | | | 60 | 0.00218 | 95 | 0.000058 | | |
| 6 | | | | | 94.8 | 0.0216 | | |
| 7 | | | | | 98.076 | 0.025 | | |
| 8 | | | 61 | 0.01483 | 97.0 | 0.0216 | 215 | 0.088 |
| 9 | 46.00 | 0.001 | | | 95.5 | 0.00213 | 197.8 | 0.001 |
| 10 | | | 61.75 | 0.01483 | 98.88 | 0.0216 | 199.16 | 0.0001 |
| 11 | 46.34 | 0.00235 | 60.021 | 0.01981 | 97.0 | 0.04678 | 209.67 | 0.03096 |
| 12 | 42.00 | 0.0088 | | | 93.80 | 0.0191 | | |
| 13 | 45.2-46.2 | | 60-63.8 | | 92.7-99 | | 197.8-217.1 | |
| 14 | 45 | 0.0089 | 62.4 | 0.01483 | 98 | 0.0216 | 200 | 0.08 |
| 15 | 45.2 | 0.01 | 63.8 | 0.01483 | 98.0 | 0.0216 | 205.0 | 0.05 |
| Range above | 42-46.3 | .01-.001 | 59.8-63.8 | 1e-5 - .019 | 92.7-98.88 | 5.8e-5 - .047 | 197-215 | .0001-.088 |
| Range- Reed | 45.2-46.2 | | 60-63.8 | | 92.7-99 | | 197.8-217.1 | |
| NEW UW | 44.4 | 0.01 | 62.1 | 0.02 | 98.5 | 0.033 | 204 | 0.04 |