



Layered Synthetic Diffractors and the “Invalidity of the Bragg Equation”

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Layered Synthetic Diffractors
Layered Synthetic Materials
Layered Diffraction Elements
Multilayered Diffractors
“Pseudo Crystals”

Pseudocrystals/LSMs

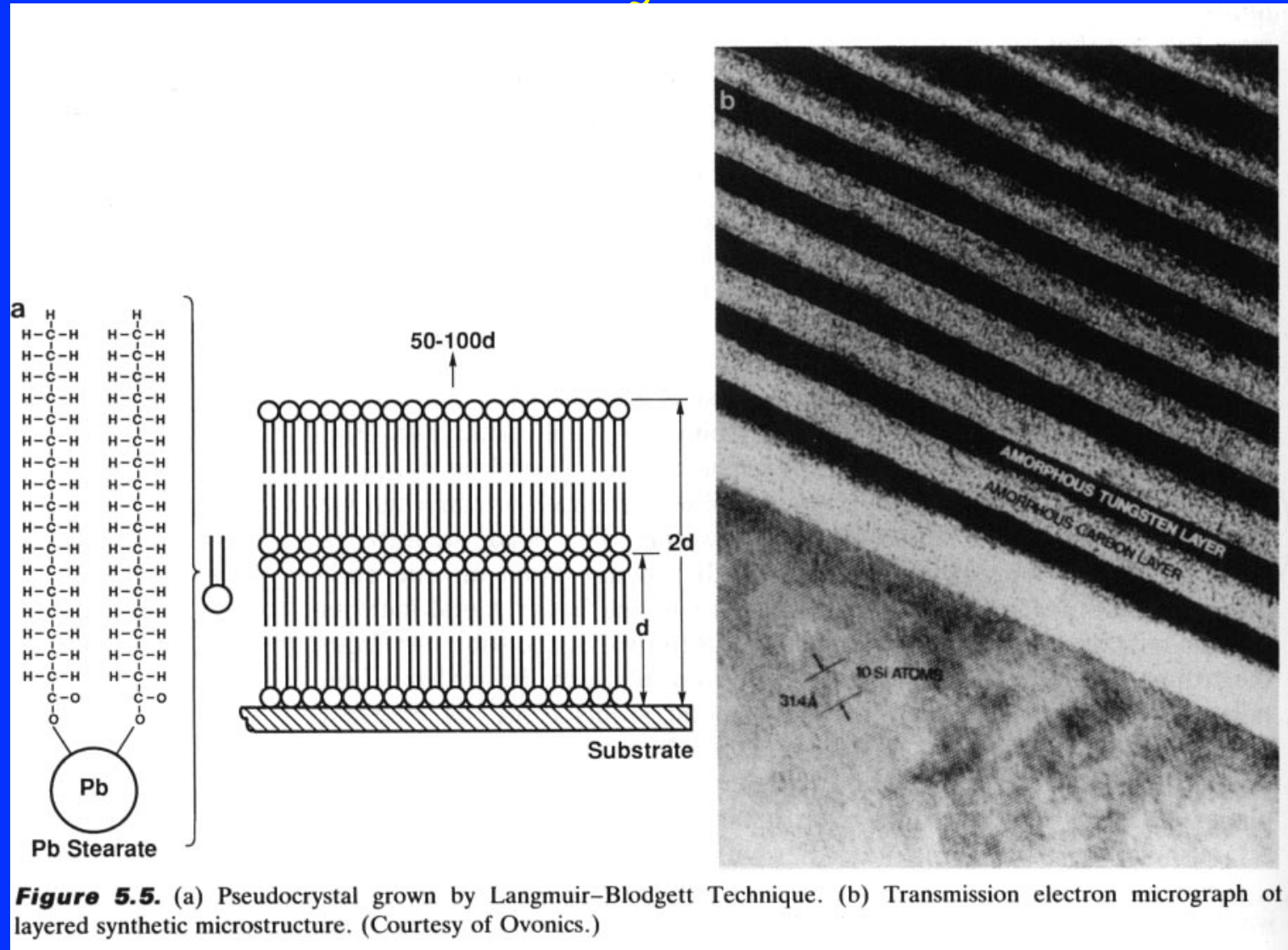


Figure 5.5. (a) Pseudocrystal grown by Langmuir-Blodgett Technique. (b) Transmission electron micrograph of layered synthetic microstructure. (Courtesy of Ovonic.)

Issues with layered synthetic diffractors:

- ☺ They give high count rates
- ☺ Peak/background ratios are good
- ☺ 2nd order peaks are weak and 3rd and above >99% suppressed
- ☺ Peak shift/shape effects muted
- ☹ Poor spectral resolution (wide peaks) with interferences common
- ☹ Relative difference of refraction of longer wavelength (1st order) lines compared with higher order (shorter wavelength) interferences, is greater here than in the smaller 2d crystals, making Siegbahn's modification of Bragg's Law critical

Crystals and LSMs on one Electron Microprobe (UW-Madison SX51 #485)

Crystal	name	formula	orientation	2d (Å)	k	Approx range(Å)
LIF	Lithium fluoride		200	4.0267	0.000058	.8 - 3.0
PET	Pentaerythritol	C(CH ₂ OH) ₄	002	8.75	0.000144	2.2 - 7.1
TAP	Thallium acid phthalate	TIHC ₈ H ₄ O ₄	1010	25.745	0.00218	6.5 - 20
LDE 45-PC0		W-Si		45.0	0.021	11. - 36.
LDE 60-PC1		W-Si		60	0.01	15 - 48
LDE 98-PC2		Ni-C		98	0.002	25-80
LDE 198-PC3		Mo-B ₄ C		200	0.05	50-160

A historical note:

12. The Invalidity of the Bragg Interference Equation in Measurements of Greater Precision

The relation between the wave-length and the angle of reflection in the various orders, which was derived by Bragg in the above elementary way, was tested by him, using his ionization spectrometer, and was found to hold within the limits of accuracy attained. In particular, he was able to show that by reflection of a given wave-length in different orders, the function

$$\frac{\lambda}{2d} = \frac{\sin \phi_n}{n},$$

where ϕ_n represents the angle of reflection in the n th order, is a constant.

The author has endeavoured to increase as far as possible the accuracy of measurement in X-ray spectroscopy, and with this in view has constructed suitable types of spectrographs. After the precision of measurement had been raised to a considerable extent it was permissible to make a test to see whether or not the Bragg relation, when applied to calculate wave-lengths from angles measured experimentally, would still remain valid. The very first trials made in this direction by W. Stenström showed unequivocally, that at least with certain crystals, and especially for longer wave-lengths, the accepted relation could not be strictly true. The above function, which, when one and the same monochromatic radiation is used, was thought to be constant, showed a divergence from this simple relation; and this divergence, although small, seemed to lie outside the limits of error. However, the deviations from the constant value found by Stenström were very small, and did not permit any certain conclusions as to the manner of variation.

Since it has become possible recently to extend the accuracy of measurement still further, the author has succeeded in demonstrating the invalidity of the Bragg relation also in the case of shorter wave-lengths. With the apparatus last indicated E. Hjalmar has now investigated this question thoroughly, and has published a very good series of measurements, which suffice to make the effect quite evident. His measurements in spectra of very high orders were especially conducive to his great success. In certain cases he obtained photographs which were well capable of measurement even in the tenth order.

In the following table, taken from Hjalmar's doctor's dissertation, are assembled the values of $\log \frac{\sin \phi_n}{n}$ for various orders n as they were obtained from the measurements. The table shows the spectral line used in each case. Only single lines without fine structure were used.

THE SPECTROSCOPY OF X-RAYS

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After the Braggs published their results in 1913-14, Siegbahn, Stenstrom and Hjalmar found that higher resolution spectroscopy indicated that while Braggs' equation was very close for 1st order lines, there were systematic deviations with higher order line locations.

TABLE 2.

$\log \frac{\sin \phi_n}{n}$ from the spectral lines :

Order.	W $L\beta_1$.	Cu $K\alpha_1$.	Fe $K\beta_1$.	Fe $K\alpha_1$.	Va $K\alpha_1$.	Sc $K\alpha_1$.	Sn $L\beta_1$.	K $K\alpha_1$.
1	8.9269523	9.0065961	9.0635972	9.1059168	9.2174174	9.3003512	9.3482412	9.3917609
2	2986	0186	0590	3109	2169973	0059	3478718	3780
3	1675	0059561	0629822	2218	8777	2998780	7110	2741
4	1032	9043	9360	1674	7914	8130		
5	0362	8837	8975	1298	7639			
6	0009	8618		1062				
7		8400						
8		8330						
10	8.9259594							

In order that the regularity of the variation may better be seen, the values are shown graphically in Figs. 18A-18D. From these curves it may be concluded that the value of $\log \frac{\sin \phi_n}{n}$ decreases with increasing order, and appears to approach a limiting value. That the above equation of Bragg cannot be quite correct from the theoretical point of view was first pointed out by C. G. Darwin, who gave a detailed calculation of the phenomenon of the reflection of X-rays. A more profound theory, on the same basis as that given in the treatment of the diffraction of X-rays by Laue, has been worked out by P. P. Ewald. In their main results the theories of Darwin and Ewald are identical. In both of them the extension of the simpler treatment is due to the necessity of taking the mutual action of the vibrating particles into consideration.

If this mutual action be considered, the observable angle of reflection ϕ_n in the n th order has a value slightly different from that ($\bar{\phi}_n$) given by the Bragg equation :

$$n\lambda_0 = 2d \sin \bar{\phi}_n, \quad (17)$$

where λ_0 = wave-length in vacuum (or air).

The theory also shows that with a crystal of sufficient thickness there is total reflection for a small region $\Delta\phi_n$ on either side of the angle ϕ_n . In many cases the Bragg angle ϕ_n falls quite outside of this region $\phi_n \pm \Delta\phi_n$. The value

$$\bar{\phi} - \phi_n \quad (18)$$

is a measure of the deviation from the Bragg formula. The theoretical results give for this deviation the formula :

$$\bar{\phi}_n - \phi_n = \frac{2}{\Omega \sin 2\phi_n}, \quad (19)$$

where
$$\frac{1}{\Omega} = \frac{e^2}{2\pi c^2 m} \sum_i \frac{N_i}{v_i^2 - v^2}. \quad (20)$$

[e and m are the charge and the mass of the electron respectively, N_i the number of electrons per unit volume with the natural frequency v_i , and v is the frequency¹ of the incident radiation.]

By suitable transformation of the above equations, we obtain

$$\log \frac{\sin \phi_n}{n} = \text{const.} + \frac{A}{n^2}, \quad (21)$$

where
$$A = -\frac{4d^2}{\lambda_0^3 \Omega}. \quad (22)$$

The negative sign is here chosen in the expression for A , because Ω itself is negative. If we compare the experimental value of $\log \frac{\sin \phi_n}{n}$

$$^1 v = \frac{1}{\lambda}.$$

with the expression found for it in Ewald's theory we see that the general agreement is surprisingly good. This appears most readily from the graph of the function A/n^2 in Fig. 18D, in which the form of the curve is very like those of the experimental curves in Figs. 18A, 18B and 18C.

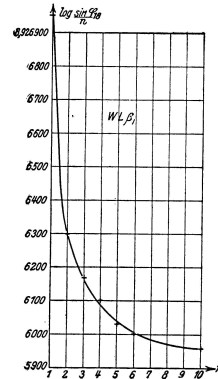


FIG. 18 A.

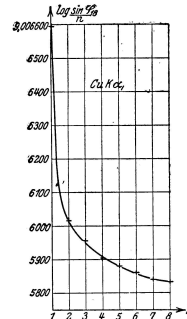


FIG. 18 B.

Equation (21) is of fundamental importance. The portion of the right-hand side denoted by "const." is, indeed, nothing else than $\log \frac{\lambda_0}{2d}$, and if we substitute ordinary logarithms and solve the equation for λ_0 we obtain

$$\log \lambda_0 = \log 2d + \log \frac{\sin \phi_n}{n} - \frac{A'}{n^2}, \quad (23)$$

where $A' = A \log e$.

The simple Bragg relation gave

$$\log \lambda_0 = \log 2d + \log \frac{\sin \bar{\phi}_n}{n}.$$

The slight correction term A'/n^2 becomes smaller and smaller as the number of the order increases, and thus for higher orders the corrected equation (23) goes over into the simple Bragg expression.

If λ_{Br} is the value of the wave-length which is obtained by using the simple Bragg formula when the observed angle ϕ_n is introduced in it :

$$n\lambda_{Br} = 2d \cdot \sin \phi_n, \quad (24a)$$

the equations (17) and (19) give

$$\lambda_0 = \lambda_{Br} \left[1 + \frac{1}{\Omega \sin^2 \phi_n} \right].$$

Introducing the refractive index μ , or better still the value δ , for the small difference $1 - \mu$ in the following relations :

$$\delta = 1 - \mu = -\frac{1}{\Omega} = \frac{e^2}{2\pi c^2 m} \sum_i \frac{N_i}{v_i^2 - v^2}, \quad (20b)$$

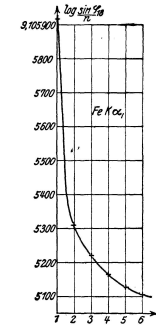


FIG. 18 C.

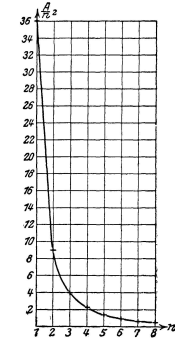


FIG. 18 D.

we obtain for the connection between the true wave-length and that calculated from the simple Bragg law :

$$\lambda_0 = \lambda_{Br} \left[1 - \frac{4d^2 \delta}{n^2 \lambda_0^2} \right]. \quad (24b)$$

This shows that—if this theory is in accordance with empirical data—we have only to multiply the calculated wave-lengths λ_{Br} by the factor

$$\left[1 - \frac{4d^2 \delta}{n^2 \lambda_0^2} \right],$$

to get the true wave-lengths. It is not difficult to find a good approximate value for this factor. In the expression for δ in equation (20b), the values of v_i are negligible for most of the electrons, as compared with v . If we neglect them, and note the density ρ of the crystal, we get the approximate expression :

$$\frac{\delta}{\lambda_0^2} = 1.35\rho \cdot 10^{10}.$$

This gives the multiplying factor the following value :

$$\left[1 - 5.4 \frac{\rho d^2}{n^2} \cdot 10^{-6} \right],$$

where d is in Å.U.

The correction resulting from this formula is proportional to

- (1) the density of the crystal,
- (2) the square of the lattice-constant,

and inversely proportional to

- (3) the square of the order.

Hence, by using a slightly smaller lattice-constant d' given by

$$d' = d \left[1 - 5.4 \frac{\rho d^2}{n^2} \cdot 10^{-6} \right],$$

instead of the true d (which represents the distance in Ångströms between the reflecting atomic planes), we get the true wave-lengths by a formula similar to the Bragg equation,

$$n\lambda_0 = 2d' \sin \phi_n. \quad (24c)$$

Or replacing d' we have the familiar equation

$$n\lambda = 2d \sin\theta (1 - k/n^2)$$

k is refraction factor, n is order of diffraction

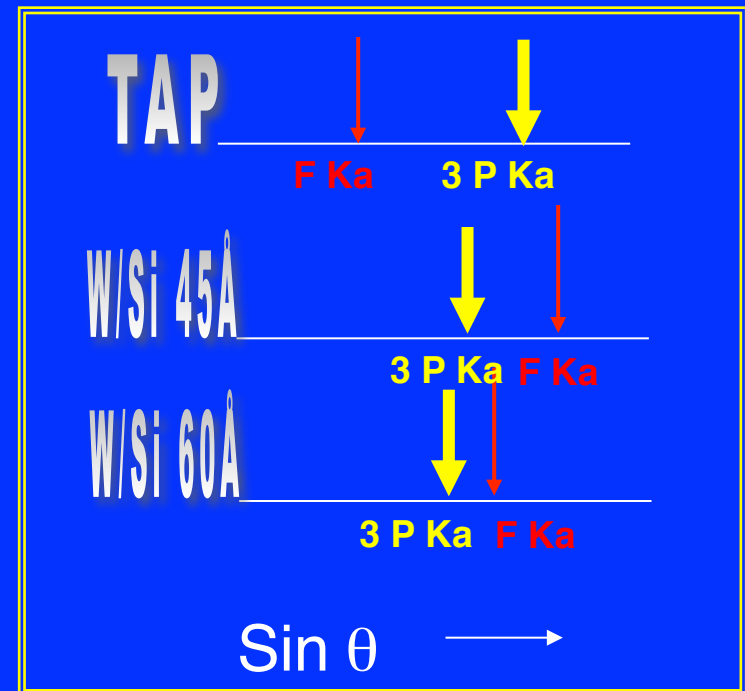
“So what difference does this equation make,” you are asking.

I came upon this by accident, in 1998, trying to answer a researcher’s persistent question “How do you know that the 3rd order P ka peak is totally attenuated by the LDE?”

I did wavescans in both TAP and LDEs, but I was confused — on TAP, the ^3P marker was to the right of F, but on the LDE, ^3P was to the left of F.

This made no sense to me.

This figure shows schematically the relative positions of the markers for F Ka and 3rd order P Ka on a wavescan (in $\sin \theta$ or angstroms, increasing to the right)



F Ka=18.32 Å

P Ka=6.157Å

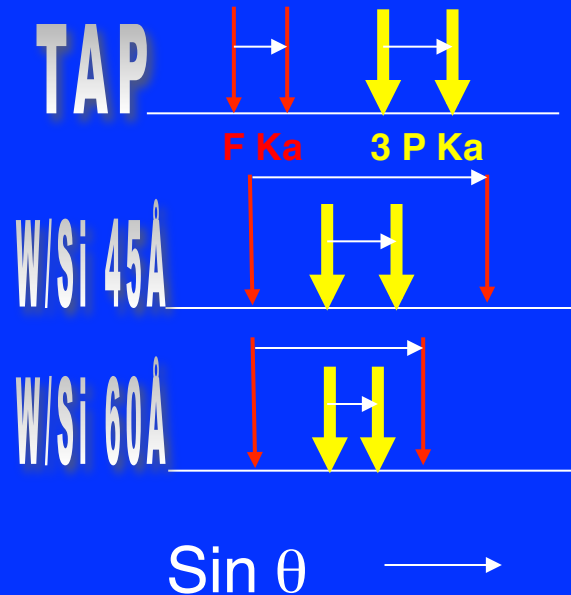
^3P Ka= 18.471Å

“The Refraction Effect” ... or the Need to use the Corrected Bragg Equation

I emailed Stephen Reed. He explained this “cross over” effect being due to the refraction effect...which now I know is taken into account by the Bragg Equation modified by Siegbahn.

Here are the calculations that demonstrate the “cross over” for the LDEs. Key is the value of $1 - k/n^2$, which is the divisor (=modifier) of the theoretical position.

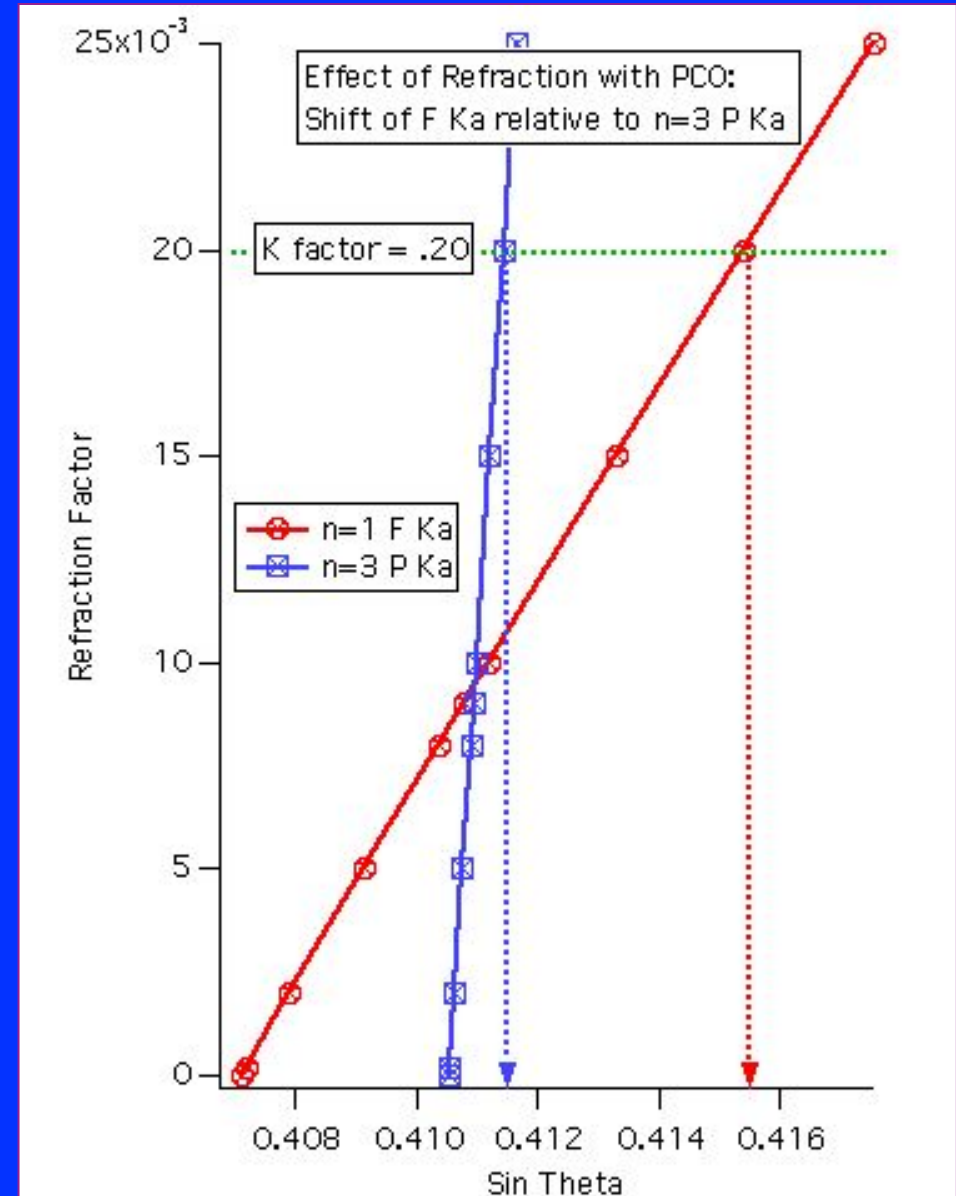
F 18.32 Å	P 6.157Å	3*P 18.471Å		
				Reversed
	"Braggs Law"	$1 - (k/n^2)$	Siegbahn	Order?
TAP	F=.71159	$1 - .002 = .998$	0.71302	
2d=25.745				No
K=.002	3P=.71746	$1 - .002/9 = .99978$	0.71762	
W/Si 45Å	F=.40711	$1 - .02 = .98$	0.41602	
2d=45Å				Yes
K=.02	3P=.41046	$1 - .02/9 = .9978$	0.41136	
W/Si 60Å	F=.30033	$1 - .01 = .99$	0.30336	
2d=61Å				Yes
K=.01	3P=.30280	$1 - .01/9 = .9989$	0.30314	



Or look at the effect of varying the refraction factor K on the W/Si 45Å

F 18.32 Å	P 6.157Å	3*P 18.471Å		Reversed
"Braggs Law"		$1-(k/n^{**2})$	Siegbahn	Order?
TAP	F=.71159	1-.002=.998	0.71302	
2d=25.745				No
K=.002	3P=.71746	1-.002/9=.99978	0.71762	
W/Si 45Å	F=.40711	1-.02=.98	0.41602	
2d=45Å				Yes
K=.02	3P=.41046	1-.02/9=.9978	0.41136	
W/Si 60Å	F=.30033	1-.01=.99	0.30336	
2d=61Å				Yes
K=.01	3P=.30280	1-.01/9=.9989	0.30314	

At what value K would F Ka and 3rd order P Ka fall on exactly the same wavelength for the 45Å LDE?



How do you know what the $2d$ and k are?? You can trust someone else....or figure it out yourself.

In July 2003 I spoke with Frank Hatfield of Osmic and asked how they calculate $2d$. He said they certify that any multilayer is within $\pm 3\%$ of its specified $2d$. The $2d$ is found by measuring the position of the 'main X-ray' of the multilayer and solving for the $2d$ in the Bragg equation. I asked about how they determined 'K factor' and he had no answer.

Well, the K factor does matter — although one could get along with erroneous values as long as there is no inquisitiveness about higher order interferences on ones layered synthetic diffractors.



Here is my first cut at figuring out the 2d and K values of my LDEs: the assumptions are that the crystals have been reasonably well aligned by the Cameca builder. There are two unknowns, and below the K is varied to find an average 2d that is similar to the value marked on the side of the LDE.

		Peak Meas	averages	Bearden	"2d"	NIST	k=0	k=.002	k=.01	k=.02	k=.021	k=.05	Cameca λ	"2d"
PC2	O	### # # #	0.24741	23.62	95.47	23.71	95.83	96.02	96.80	97.78	97.88	100.87	24.14038	97.5724
100Å	N	### # # #	0.33324	31.60	94.83	31.60	94.84	95.03	95.80	96.78	96.88	99.83	32.41438	97.2711
nom	C	### # #	0.46124	44.70	96.91	44.00	95.40	95.59	96.36	97.35	97.45	100.42	44.82466	97.1836
	B	###	0.71390	67.60	94.69	67.00	93.85	94.04	94.80	95.77	95.87	98.79	67.64049	94.7478
								average						
								95.17		96.92				
PC1	F	### # #	0.30937	18.32	59.22	18.31	59.18	59.29	59.77	60.38	60.45	62.29	18.3193	59.2142
60Å	O	### # # #	0.39302	23.62	60.10	23.71	60.32	60.45	60.93	61.56	61.62	63.50	24.14038	61.4225
nom	N	### # # #	0.52229	31.60	60.50	31.60	60.51	60.63	61.12	61.75	61.81	63.70	32.41438	62.0626
	C	### # # #	0.72987	44.70	61.24	44.00	60.29	60.41	60.90	61.52	61.58	63.46	44.82466	61.415
								average						
								60.68						
PC0	Na	### # #	0.26892	11.91	44.29	11.91	44.29	44.37	44.73	45.19	45.24	46.62	11.909	44.2851
45Å	F	### # #	0.41619	18.32	44.02	18.31	43.99	44.08	44.43	44.89	44.93	46.30	18.3193	44.0163
nom	O	### # #	0.53731	23.62	43.96	23.71	44.12	44.21	44.57	45.03	45.07	46.45	24.14038	44.9282
	N	### # # #	0.71954	31.60	43.92	31.60	43.92	44.01	44.37	44.82	44.87	46.24	32.41438	45.0488
										average				
										45.03				
PC3	Be	###	0.60820	114.00	187.44	114.27	187.89	188.26	189.78	191.72	191.92	197.77	114.27200	187.886
200Å	B	###	0.35000	67.60	193.14	67.00	191.43	191.81	193.36	195.34	195.53	201.50	67.64049	193.259
nom										average				
										199.64				

xtals say on them

PC1 61.0
 PC2 95.2
 PC3 200

The next iteration is to find a 2nd order reflection near a first order line and verify that the above K value is correct.

Summary

1. For LDE' s, the precise form of Bragg' s Law as modified by Siegbahn should be understood and used.
2. The K-values can be relatively easily determined, and should be done so, both to keep the vendors honest and to have peace of mind.

