XRD Lattice Parameter

Why are Kα_1 and Kα_2 peaks resolved at high angles?

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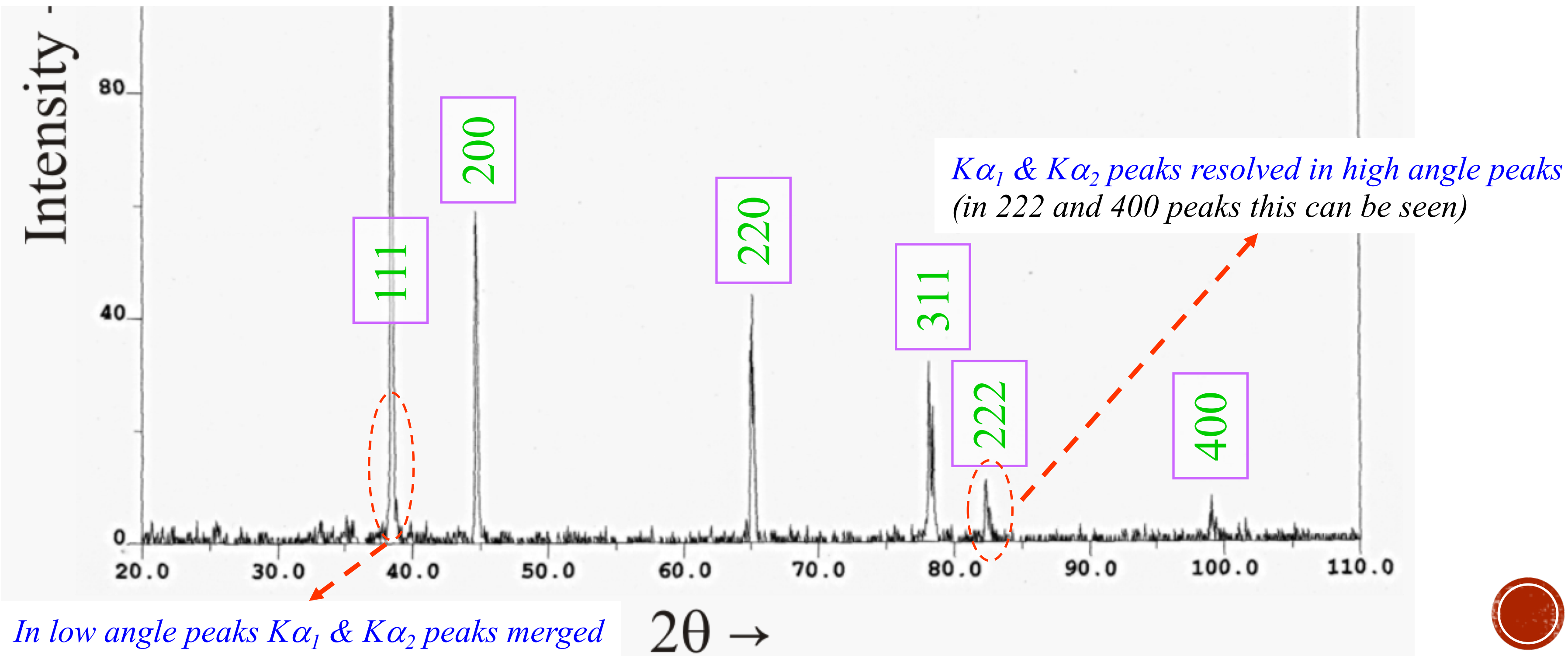
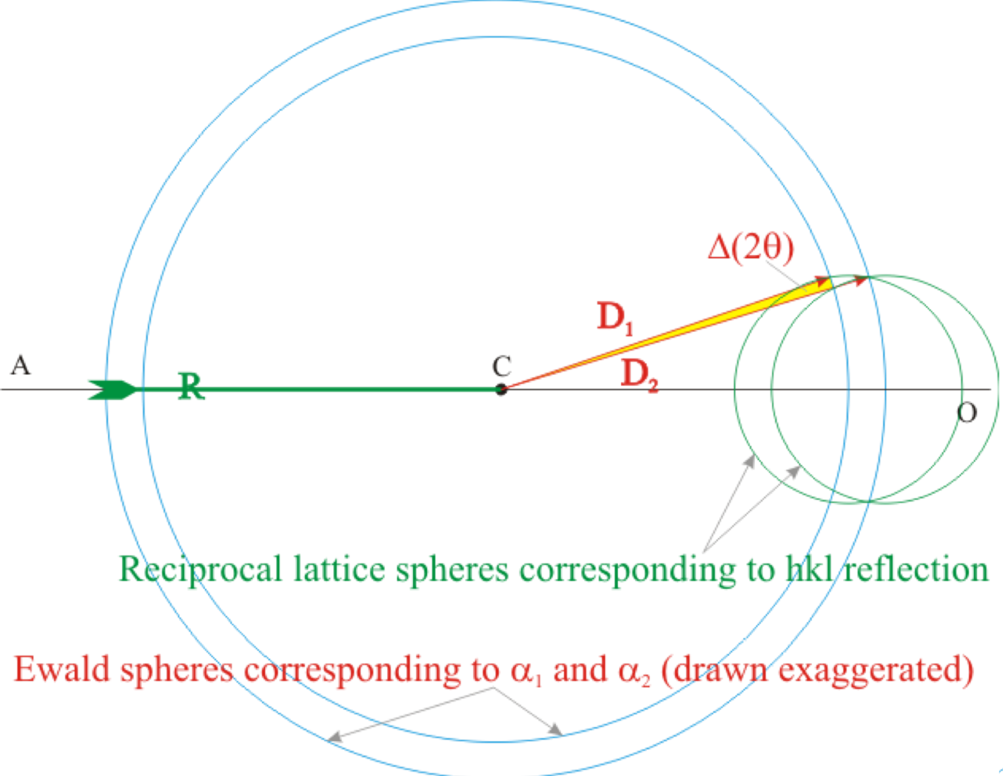
Which 'Line' to use for lattice parameter calculation?

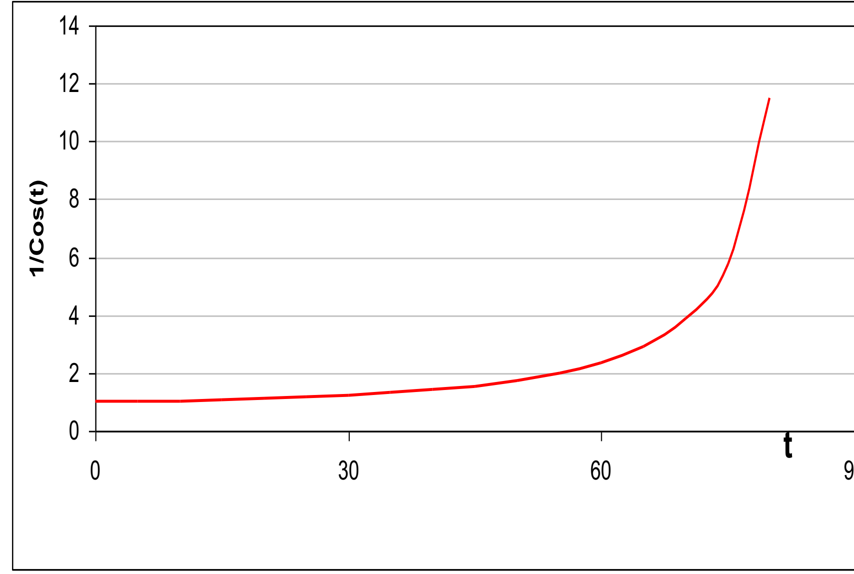
- At higher Bragg angles the Kα_1 and Kα_2 lines are resolved (reason shown in the next slide)
- Typically we use only the Kα_1 lines for the calculation of lattice parameter
- The error in the calculation of lattice parameter decreases with increasing angle → hence the high angle peaks should be used for lattice parameter calculation (instead of taking an average over all peaks or taking any of the intense low angle peaks)

Why are Kα_1 and Kα_2 peaks resolved at high angles?

- The Kα_1 ($Cu_{K\alpha1}$ = 1.540598 Å) and Kα_2 ($Cu_{K\alpha2}$ = 1.54439 Å) lines differ slightly in wavelength. Hence, in principle two separate peaks should be seen in the diffraction pattern.
- Usually, at low angles these peaks are merged (i.e. seen as a single peak) and at high angles these peaks are resolved (seen as two separate peaks). *The question is why?*
- This can be understood in terms of the variation of θ with λ *(as in this case λ is not fixed)* and the graphical (Ewald sphere) construction (upcoming slides).





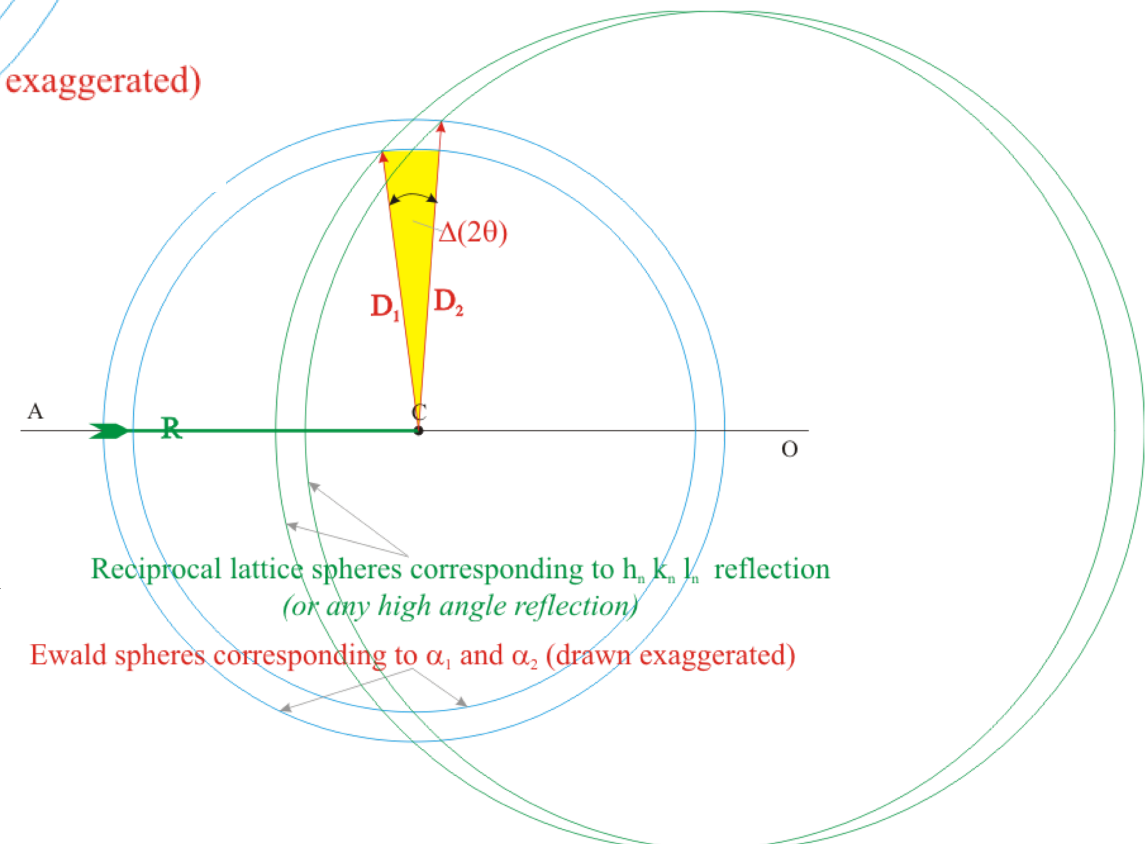


$$n\,\lambda = 2\,d\,Sin\theta \qquad \frac{d\lambda}{d\theta} = 2\,d\,Cos\theta$$

$$\frac{d\theta}{d\lambda} = \frac{1}{2\,d\,Cos\theta}$$

- α_1 and α_2 differ slightly in wavelength
- The difference in the diffracted angle $\Delta\theta$ increases with an increasing angle of diffraction θ (for a given $\Delta\lambda$). Plot of variation as above.
- Hence, the α_1 and α_2 peaks are resolved at high angles

Actually, the variation in 2θ is to be seen

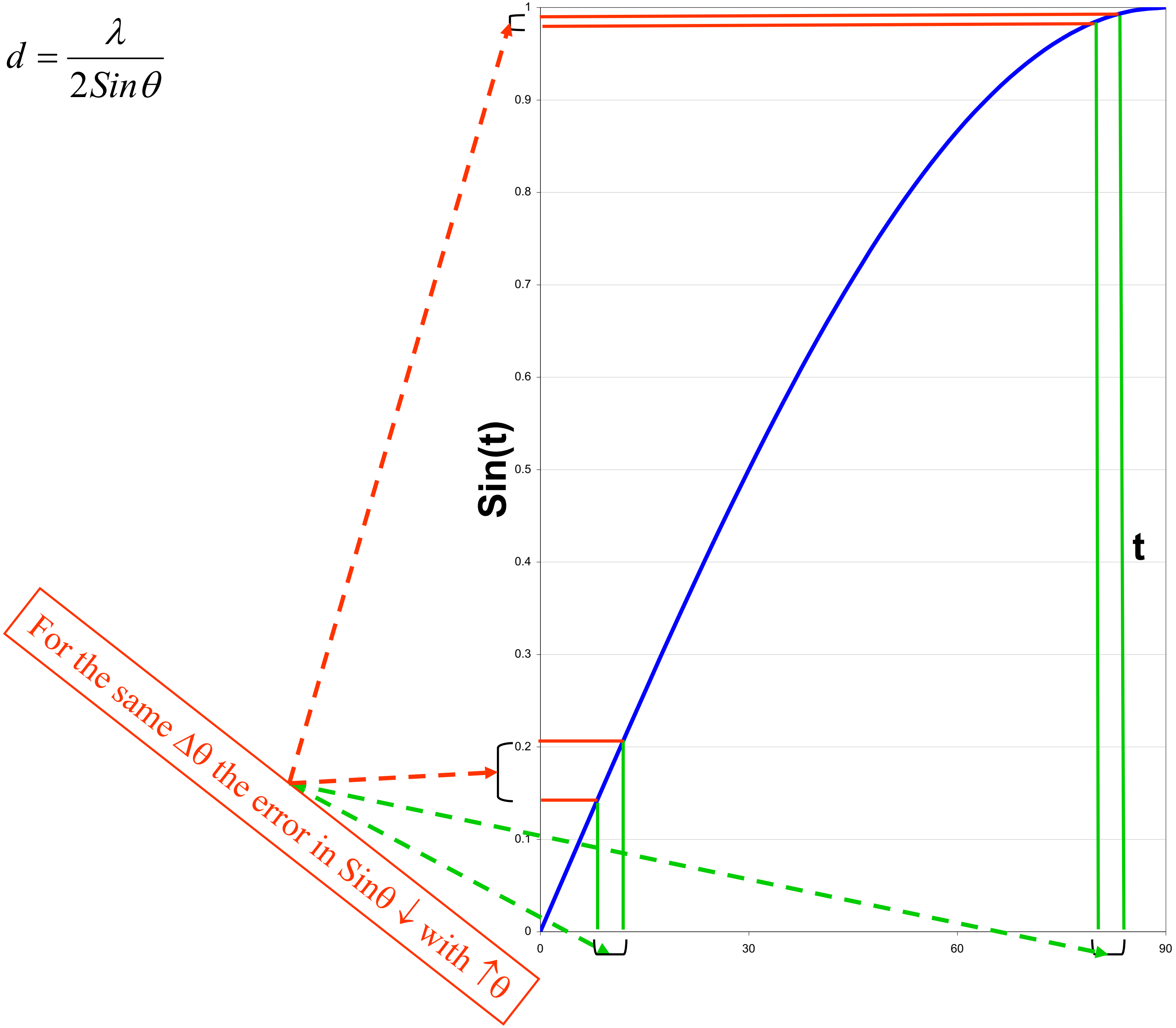


Which ‘Line’ to use for lattice parameter calculation?

- Typically we use only the $K\alpha_1$ lines for the calculation of lattice parameter. And this can be done at high angles as the $K\alpha_1$ & $K\alpha_2$ lines are resolved at high angles.
- The error in the calculation of lattice parameter decreases with increasing angle → hence the high angle peaks should be used for lattice parameter calculation (instead of taking an average over all peaks or taking any of the intense low angle peaks) (as shown in slides to follow).

Let us calculate the error in d spacing as a function of the angle of diffraction

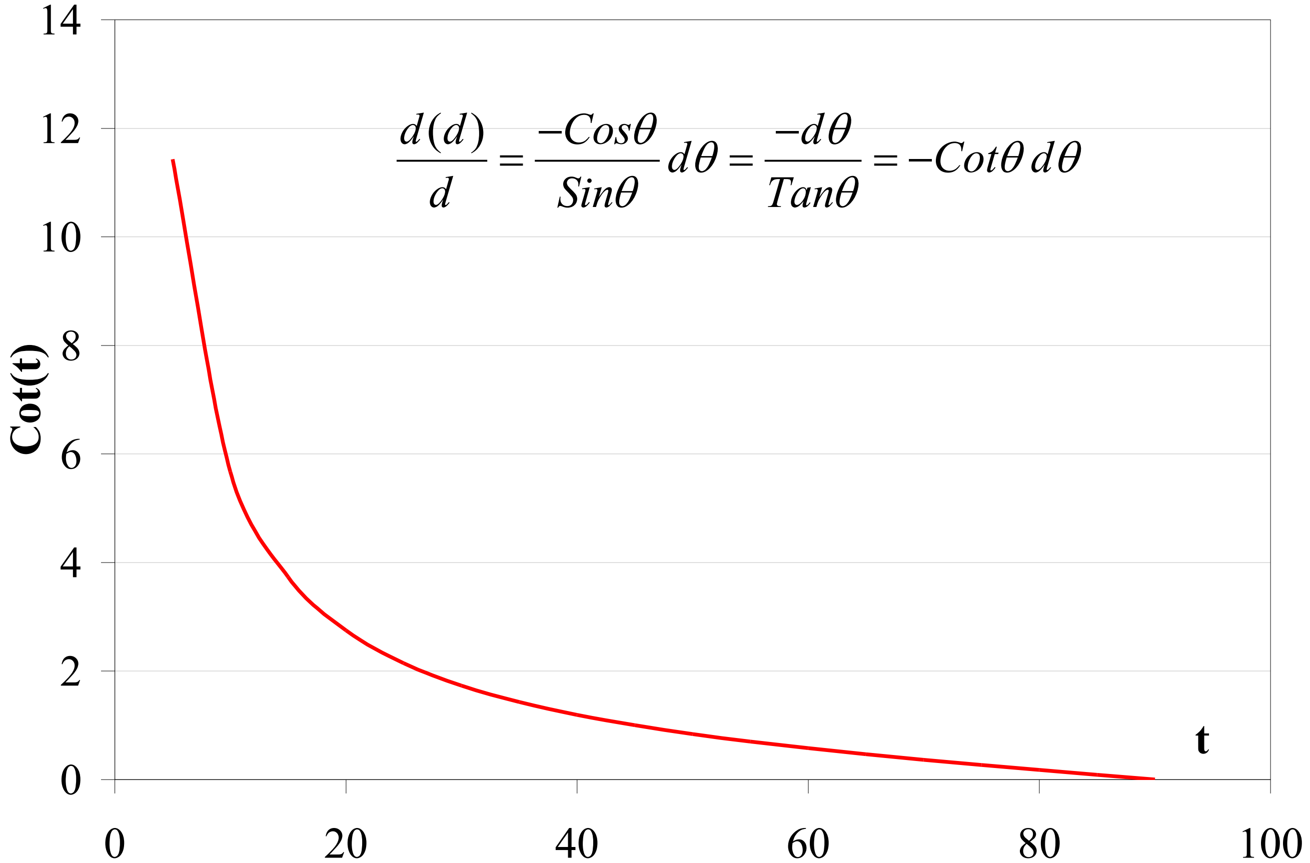
$$d = \frac{\lambda}{2Sin\theta}$$



$$\frac{d(d)}{d\theta} = \frac{-\lambda Cos\theta}{2Sin^2\theta}$$

$$\frac{d(d)}{d} = \frac{-Cos\theta}{Sin\theta} d\theta = \frac{-d\theta}{Tan\theta}$$

Error in d spacing



Error in d spacing decreases with θ

→ hence high angle peaks have to be used for lattice parameter calculation

Determination of Lattice parameter from 2θ versus Intensity Data

n	2θ	θ	Sinθ	Sin² θ	ratio	Index	a (nm)
1	38.52	19.26	0.33	0.11	3	111	0.40448
2	44.76	22.38	0.38	0.14	4	200	0.40457
3	65.14	32.57	0.54	0.29	8	220	0.40471
4	78.26	39.13	0.63	0.40	11	311	0.40480
5*	82.47	41.235	0.66	0.43	12	222	0.40480
6*	99.11	49.555	0.76	0.58	16	400	0.40485
7*	112.03	56.015	0.83	0.69	19	331	0.40491
8*	116.60	58.3	0.85	0.72	20	420	0.40491
9*	137.47	68.735	0.93	0.87	24	422	0.40494

Decreasing error

* → α_1 , α_2 *peaks are resolved (*α_1 *peaks are listed)*

Others methods exist for precise lattice parameter measurement (than just taking a single value)!

$$1.54 = 2\, d_{422}\, Sin\theta_{422} = 2\frac{a}{\sqrt{24}}0.93$$

$$a_{Calculated\ \ from\ the\ 422\ line} = 4.0494\,\overset{o}{\mathrm{A}}$$

References:

MATERIALS SCIENCE & ENGINEERING: A Learner's Guide,

Anandh Subramaniam,

http://home.iitk.ac.in/~anandh/E-book.htm.