1. How does F_{hkl} change for centrosymmetric structures? Show your derivation step by step. Can the x-ray reflection intensities for centrosymmetric structures be used to directly calculate the electron density distribution?

For every atom at (x,y,z) there must be a symmetry equivalent atom at (-x,-y,-z)

Then:

$$F = \sum_{j=1}^{N/2} f\,(\exp(2\pi i\,(hx_j + ky_j + lz_j)) + \exp(-2\pi i\,(hx_j + ky_j + lz_j)))$$

$$F = \sum_{j=1}^{N/2} 2f\cos(2\pi\,(hx_j + ky_j + lz_j))$$

Thus, all Fs are REAL (not imaginary). However, the intensities still do not yield F-values directly since, for centrosymmetric structures:

$$I^{1/2} = \pm F$$

2. The diffraction pattern below was obtained from a common cubic material using CuKα radiation. Determine the Miller indices for each reflection ("index the pattern"), and thereby determine the centering type for the lattice from an inspection of the systematic absences. Calculate the lattice parameter, **a**.

   To index the pattern, guess the (hkl)'s for the first two or three reflections for P, I, and F cubic, and calculate the corresponding **a** values for these reflections. Since this cubic material has a single lattice parameter, the assignment of indices which gives **a** values which are very close to each other is the correct one. You will run into an additional problem here; in attempting to solve the problem, do not use h,k,l values higher than 5. In indexing the pattern, remember that the objective is to find some set of indices (hkl) that gives essentially the same lattice parameter for all reflections.

d(Å)	(hkl) for P	(hkl) for I	(hkl) for F

3.157 try primitive ——>

3.157	(100)	3.157
1.931	(110)	2.731

1.931
1.647
1.366 try I cubic ——>

3.157	(110)	4.465
1.931	(200)	3.862

1.253
1.1150 try F cubic ——>

3.157	(111)	5.468
1.931	(200)	3.862

1.0512
0.9657 Since none works, there must be some additional extinctions due to glide planes and/or screw axes
0.9233
0.9105 Suppose F cubic OK, but 200 is extinct. Then
0.8637

3.157	(111)	5.468
1.931	(220)	5.462

0.8330

AHA!!! This looks promising! Further guesses give:

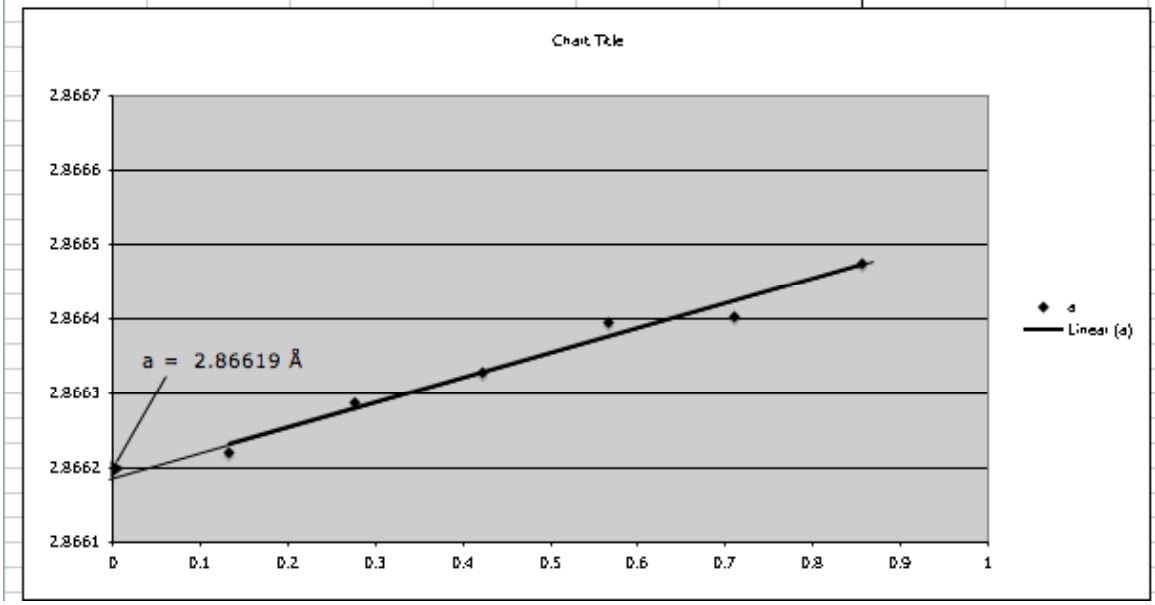
1.647	(311)	5.462
1.366	(400)	5.464

At this point, we may wish to use **a** = 5.462 Å and calculate d-values and match with the rest of the reflections

3. The most precise values of lattice parameters are those obtained for reflections which occur at high angles. In fact, all errors can be eliminated at $\theta = 90°$, and lattice parameter values generally reported are those obtained from an extrapolation of the data to $\theta = 90°$ against some function intended to make the lattice parameter variation linear. Two such functions, obtained through an extensive evaluation of systematic experimental errors, are the Bradley and Jay function, $\cos^2\theta$ (frequently used for diffractometer data, and truly linear only over the range θ = 60-90°) and the Nelson-Riley function ($\cos^2\theta/\sin\theta + \cos^2\theta/\theta$, linear over the range 30-90°θ, and used for other instrument geometries).

   Here are some observed data for α-iron. Determine the best lattice parameter to 5 decimal places by extrapolating the **a** values versus $\cos^2\theta$ in a graph. $\lambda_{CuK\alpha_1}$ = 1.5405981 Å. To index the pattern, remember that α-iron is I cubic.

theta	theta radians	sine theta	d	s	a	(cos theta)2	a
22.336	0.38983674	0.3800374	2.02690325	2	2.86647406	0.85557157	2.86647406
32.5114	0.56743096	0.5374674	1.43320144	4	2.86640289	0.7111288	2.86640289
41.1675	0.71850841	0.65826255	1.17020032	6	2.86639369	0.56669041	2.86639369
49.4742	0.86348767	0.76011344	1.01340012	8	2.8663284	0.42222756	2.8663284
58.1948	1.01569085	0.84984486	0.90639962	10	2.86628725	0.27776372	2.86628725
68.5881	1.19708815	0.93098001	0.82740665	12	2.86622072	0.13327623	2.86622072



4. For the data below, determine the weight fractions of rutile and anatase present in a mixture.

Pure rutile:

Reflection	Intensity	Background
1	102309	1508
2	47564	1453

Rutile in the mixture:

Reflection	Intensity	Background
1	36987	1486

2	17408	1439

5. A rock specimen was analyzed for α-quartz. To correct for the unknown absorption of the specimen, an internal standard was used. The internal standard was chosen as KCl because of its excellent crystallinity, relatively simple diffraction pattern, and a strong reflection which is relatively close to the strong α-quartz reflection.

   Three samples were measured: pure KCl, pure quartz and a mixture of the rock specimen with KCl. The mixture was prepared by intimately mixing 200 mg of finely ground KCl with 1000 mg of the rock, also finely ground.

   The intensities of the 3.15 Å KCl reflection and the 3.34 Å quartz reflection were measured using CuKα radiation. The data are given below.

Phase	d (Å)	μ^o	Pure compound	Mixture
quartz	3.34	35.0	48360 cps	2648 cps
KCl	3.15	124.0	19072	6160

   For all intensities, the background was 240 cps. The dead time for the counting system was 1.0 μsec.

   The correction for the dead time, τ, makes use of the following equation:

$$\text{true counts/sec} = \frac{\text{observed counts/sec}}{1 - \tau \text{ observed counts/sec}}$$

   Calculate the concentration of quartz in the rock specimen.

   Note that:

$$\frac{I_\alpha}{I_\alpha^o} = \frac{\mu_\alpha^o}{\mu} X_\alpha$$

where:

I_α^o and I_α are the intensities for the pure compound and the mixture for phase α, respectively.

μ_α^o and μ are the mass attenuation coefficients for the pure compound and the mixture, respectively.

X_α is the weight fraction of phase α in the mixture.

An equation of this type can be written for both quartz and KCl. Combining these two equations to eliminate μ, the unknown mass attenuation coefficient for the mixture:

$$X_q = X_{KCl} \frac{I_{KCl}^o}{I_q^o} \frac{\mu_{KCl}^o}{\mu_q^o} \frac{I_q}{I_{KCl}}$$

First calculate the weight fraction X_q of quartz in the diluted specimen. Then, from the value of X_q and the dilution factor, calculate the weight fraction of quartz in the original mixture.

6. MoB is $I4_1/amd$ with a = 3.110, c = 16.95 Å, and Mo and B atoms in 8e, z = 0.196 and 0.352, respectively.

   Calculate F_{001} and F_{004}.

   F_{001} = _____

   $$F_{hkl} = \sum_{j=1}^{N} f_j \exp(2\pi i(hx_j + ky_j + lz_j)).$$

   F_{004} = ?

What must be calculated?

d_{004} = _____

$(\sin\theta)/\lambda$ = _____

	0.0	0.1
Mo	38.2	32.6
	3.5	2.4

f_{Mo} = _____

f_B = _____

8e: (00z) $(0,\frac{1}{2},\frac{1}{4}+z)$ $(\frac{1}{2},0,\frac{3}{4}-z)$ $(\frac{1}{2},\frac{1}{2},\frac{1}{2}-z)$

F_{004} = _____

7. β-Np is $P42_12$ with a = 4.897, c = 3.388 Å, and Np in 2a ((000) and $(\frac{11}{22}0)$) and 2c ($(0\frac{1}{2}z)$ and $(\frac{1}{2}0\bar{z})$), z = 0.375. Find I_{101} for CuKα radiation. Ignore absorption and temperature factor.

f calculation:

$(\sin\theta)/\lambda$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7
f	93	87	78	69	60	53	48	44

F calculation:

What is p?

LP calculation:

I calculation: