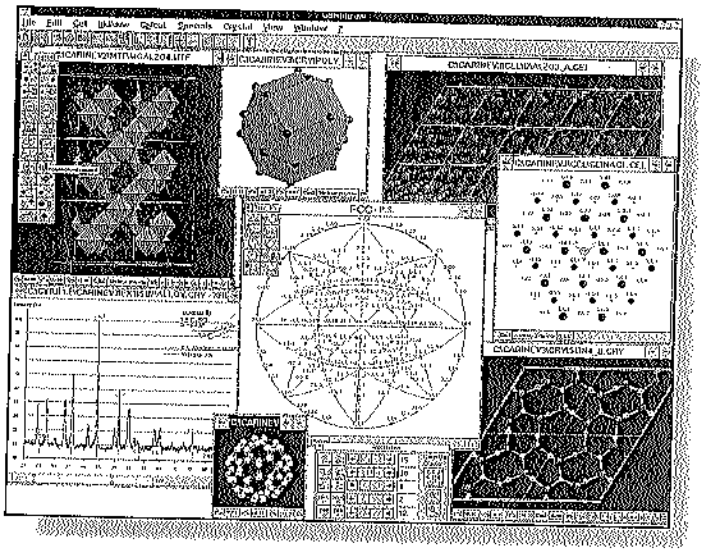
The crystallographic software for research and teaching

CaRIne Crystallography 3.0



CaRIne Crystallography for Microsoft Windows

CaRIne Crystallography version 3.0 deals interactively with several geometric visualizations of crystals : real lattices in 3D, reciprocal lattices in 3D and 2D, stereographic projections, X-Ray diffraction patterns (XRD). These options are commonly treated in several softwares. CaRIne unifies them into a nice pleasant interface for simplicity and efficiency. Moreover, thanks to this unification, CaRIne can expose clearly the relationships between these graphical representations. This is greatly appreciated for teaching purposes.

CaRIne is currently used in more than 300 labs over 18 countries, for teaching and research in the chemistry and materials science fields.

Real Lattices

- data base of structures : motifs, unit cells, crystals. Every step of the work can be saved. More than 500 example files.
- atoms and ions are defined with access to a periodic table.
- the 14 Bravais' lattices.
- the 230 space groups.
- graphics : perspective, shading, compact view or all degree of "ball and sticks".
- texture : visualization of the crystal orientation relatively to the rolling plane and direction.
- defects : vacancies, interstitials, substitutions, displacements, anti-sites.
- interactive geometric calculations : every angle and distance are obtained with the mouse.
- definition of planes and directions with the mouse.
- calculation lists : interplanar distances, structure factors, inter planar angles, interatomic distances.
- use in 2D is possible (useful for teaching).
- study of the site environment (shells).
- coordination polyhedrons from the selection of the central atom with the mouse ! CaRIne can also search automatically equivalent polyhedrons in the structure.

Reciprical Lattices

- visualization in three dimensions. Radii of nodes can be set pro portionally to the structure factor computed from Z.
- visualization in two dimensions : plane cut of the 3D reciprocal lattice from the definition of the zone axis.
- functions to help interpreting electronic diffraction patterns.

Stereographic projections

X-Rays diffraction patterns

- calculation of peak positions and intensities (CaRIne knows atomic scattering factors).
- possibility to mix powders.
- importation of experimental / reference data (θ-int. ASCII file).

Interactivity between the diverse representations

- association of real lattices, epitaxial relations.
- visualization of orientation relationships between real and reciprocal lattices.
- simultaneous rotations of the real lattices, reciprocal lattices and stereographic projections. For example, stereographic projection can be used to orientate the real and reciprocal lattices.
- superpositions of stereographic projections of different structures.
- continuous re-calculations of the XRD, reciprocal lattice and stereographic projection. For example, it is possible to add an atom to the real lattice motif and see immediately the consequences on the XRD peak intensities and extinctions.

Graphics, editing drawings

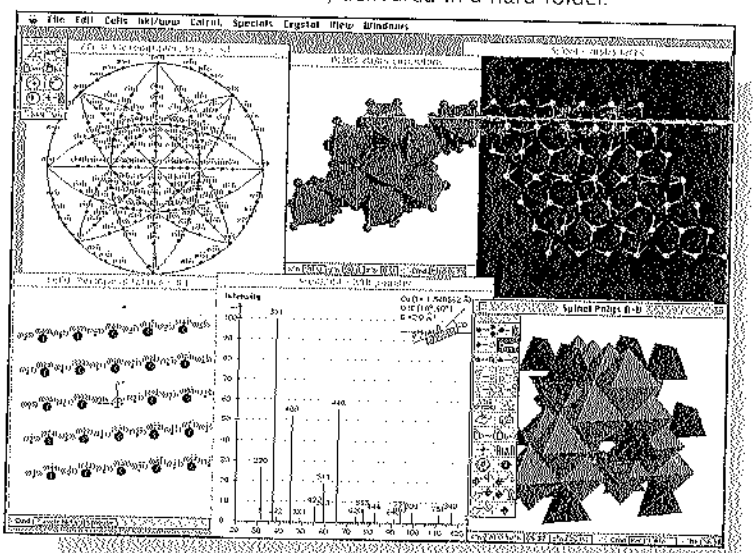
- high quality graphics.
- fast 3D rotations and projections.
- exportation of images to word processor or drawing softwares (PICT for Macintosh, WMF for Windows) : this is possible for real lattices, reciprocal lattices, stereographic projections, XRD and calculations lists.

Import / export of data

- several ASCII file formats allow the exchange (with other softwares) of : atomic positions and characteristics, space group, cell parameters, cartesian coordinates, graphic options, list of interplanar distances and angles, multiplicities, structure factors, XRD, ...).

Documentation

- includes a 120 pages user manual in English with many examples and illustrations, delivered in a hard folder.

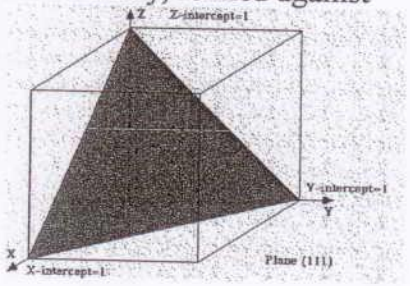


CaRIne Crystallography for Macintosh

CaRIne runs on

CHEM 481. Lab 1. Powder X-Ray Diffraction (PXRD)
What is X-ray Crystallography ?

X-ray crystallography is an experimental technique that exploits the fact that X-rays are diffracted by crystals. It is not an imaging technique. X-rays have the proper wavelength (in the Ångström range, ~10^{-8} cm) to be scattered by the electron cloud of an atom of comparable size. Based on the diffraction pattern obtained from X-ray scattering off the periodic assembly of
molecules or atoms in the crystal, the electron density can be reconstructed. Additional phase information must be extracted either from the diffraction data or from supplementing diffraction experiments to complete the reconstruction (the phase problem in crystallography). A
model is then progressively built into the experimental electron density, refined against the data and the result is a quite accurate molecular structure.



Miller Indices

- Determine the intercepts of the face along the crystallographic axes, *in terms of unit cell dimensions.*
- Take the reciprocals
- Clear fractions
- Reduce to lowest terms

For example, if the x-, y-, and z- intercepts are 2, 1, and 3, the Miller indices are calculated as:

- Take reciprocals: 1/2, 1/1, 1/3
- Clear fractions (multiply by 6): 3, 6, 2
- Reduce to lowest terms (already there)

Thus, the Miller indices are 3,6,2. If a plane is parallel to an axis, its intercept is at infinity and its Miller index is zero. A generic Miller index is denoted by *(hkl)*. If a plane has negative intercept, the negative number is denoted by a bar above the number. *Never alter negative numbers.* For example, do not divide -1, -1, -1 by -1 to get 1,1,1. This implies symmetry that the crystal may not have!

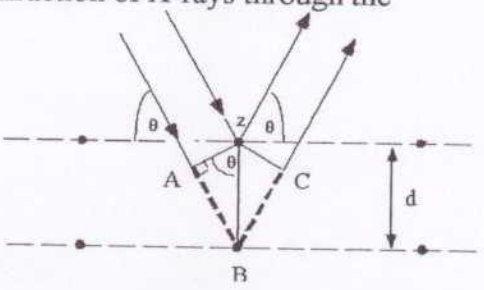
Some General Principles

- If a Miller index is zero, the plane is parallel to that axis.
- The smaller a Miller index, the more nearly parallel the plane is to the axis.
- The larger a Miller index, the more nearly perpendicular a plane is to that axis.
- Multiplying or dividing a Miller index by a constant has no effect on the orientation of the plane

- Miller indices are almost always small.

X-ray crystallography

X-ray crystallography is a technique in crystallography, the scientific study of crystals, in which the pattern produced by the diffraction of X-rays through the closely spaced lattice of atoms or ions in a crystal based on Bragg's law is recorded and then analyzed to reveal the nature of that lattice.



Bragg's Law and Diffraction:

Bragg's Law refers to the simple equation:
$n\lambda = 2d \sin\theta$

This equation is derived by the English physicists Sir W.H. Bragg and his son Sir W.L. Bragg in 1913 to explain why the cleavage faces of crystals appear to reflect X-ray beams at certain angles of incidence (theta, θ). The variable *d* is the distance between atomic layers in a crystal, and the variable lambda λ is the **wavelength** of the incident X-ray beam (see applet); n is an integer. This observation is an example of X-ray **wave interference** (Roentgenstrahl interferenzen), commonly known as X-ray diffraction (XRD), and was direct evidence for the periodic atomic structure of crystals postulated for several centuries. The Braggs were awarded the Nobel Prize in physics in 1915 for their work in determining crystal structures beginning with NaCl, ZnS and diamond. Although Bragg's law was used to explain the interference pattern of X-rays scattered by crystals, diffraction has been developed to study the structure of all states of matter with any beam, e.g., ions, electrons, neutrons, and protons, with a wavelength similar to the distance between the atomic or molecular structures of interest.

Experimental Diffraction Patterns

Reciprocal space **a***= 1/a, **b***=1/b **c***=1/c
Cubic crystal system:
Real cell dimensions:

a	5	**b**	5	**c**	5
alpha	90	**beta**	90	**gamma**	90

Reciprocal cell dimensions:

a*	0.2	**b***	0.2	**c***	0.2
alpha*	90.0000000	**beta***	90.0000000	**gamma***	90.0000000

Volume of the cell: 125 **Å**3**

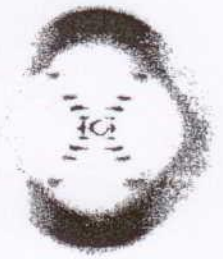
Volume of the reciprocal cell: 0.008 Å**3

Single Crystal Diffraction

Many complicated inorganic and organometallic systems have been analyzed using single crystal methods, such as fullerenes, metalloporphyrins, and many other complicated compounds. The major limitation to the quality of single-crystal data is crystal quality. Inorganic single-crystal x-ray crystallography is commonly known as small molecule crystallography, as opposed to macromolecular crystallography. Single Crystal Diffraction. Many complicated inorganic and organometallic systems have been analyzed using single crystal methods, such as fullerenes, metalloporphyrins, and many other complicated compounds. The major limitation to the quality of single-crystal data is crystal quality. Inorganic single-crystal x-ray crystallography is commonly known as small molecule crystallography, as opposed to macromolecular crystallography.

Watson, Crick, discovery of structure of DNA: What was measured by Rosalind Franklin from x-ray data

- 2 nm helical diameter
- 0.34 nm between base pairs
- 3.4 nm pitch right handed

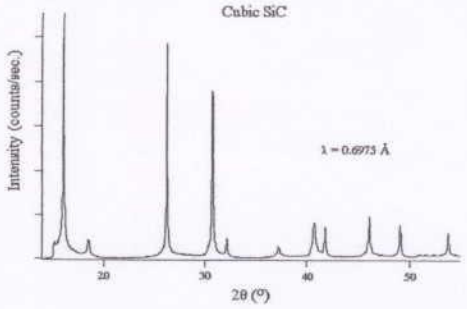


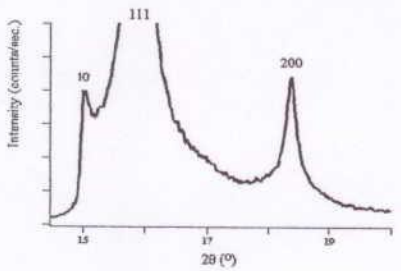
Powder Diffraction

X-ray powder diffraction finds frequent use in materials science because sample preparation is relatively easy, and the test itself is often rapid and non-destructive. The vast majority of engineering materials are crystalline, and even those which are not yield some useful information in diffraction experiments.

The pattern of powder diffraction peaks can be used to quickly identify materials (thanks to the ICCD-JCPDS pattern database), and changes in peak width or position can be used to determine crystal size, purity, and texture.

Experimental Powder Diffraction Patterns





PROCEDURE FOR DETERMINING DIFFRACTION PATTERNS AND AUTO INDEXING USING SCINTAG POWDER DIFFRACTOMETER

The procedure given describes how to run an X-ray analysis of a compound.

1. Turn on the tap by turning the nozzle counter clockwise. Then, turn on the water cooler pump.
2. Turn on the power to the spectrometer.
3. Press control power on.
4. Press X-ray off button and check the mA and kV readings. (should be 10mA and negative 10kV).
5. Press X-ray power on button.
6. Turn the computer and go to NT operating system.
7. Go to program DMSNT.
8. On the program task bar, pull down Hardware and go to Configuration.
9. Make sure the detector and sample omega are set to zero.
10. Pull down Hardware again; select Manual commands and the Goinmeter.
11. Check hardware –set next position to 40 m and then click Axis power on. After test, set back to zero.
12. Check water levels, they should be about 65°F and 70 psi.
13. Slowly turn mA and kV up using the following intervals. Each interval should be 3 minutes apart. mA-10, 16, 22, 28 and 35 kV-10, 19,28,37 and 45.
14. Prepare sample. Put sample in diffractometer and turn the light inside the machine off.
15. At computer, open Event List and set Raw file name, ID, and comments.
16. Normal Scan-start at 2° angle, stop at 80° angle, set to continuous, and set the rate of scan.
17. Before the scan starts, make sure that the interlock reset light is off.
18. Click Go FROM Top to start scan, and when the scan is finished, save to file.
19. After all the scans are finished, set the axes back to 0, 0.
20. Slowly set the mA and kV back to positive ten and negative ten using the same intervals used to turn them on.
21. Turn X-ray power off.
22. Turn the power off to the spectrometer.
23. Make sure the machine is thoroughly cooled and turn the water and the pump off.
24. Shut down the computer.

Search match of powder patterns

The procedure given describes how the search/match program was used to find similar compounds to match the different powder patterns.

1. Turn on the computer.
2. Go to program DMSNT.
3. Select a compound.
4. Run a background removal, smoothing, and correction of the compound.
5. Select the peak finder.
6. Select the search match for the compound.

Auto Indexing Procedure

The following describes how the crystallography program was used to find the unit cells of the compounds.

1. Turn on the computer.
2. Go to program DMSNT.
3. Go to open file.
4. Select a compound.
5. Run a background removal, smoothing and correction of the compound.
6. Select the peak finder and save the compound.
7. Go to analysis and select crystallography.
8. Select new report generator.
9. Set the maximum intensity to 65000.
10. Reset the peak files.
11. Select treor auto indexing and select at least five peaks.
12. Calculate.

CRYSTALLOGRAPHY RUN FOR COBALT OXIDE NANOPARTICLES

\par P-E WERNER'S TREOR90\plain\f3\fs20\cf0
\par FOR PC SYSTEMS
\par 37.532500 205
\par 43.100000 270
\par 52.240000 422
\par 57.180000 423
\par 66.234380 479
\par STOP LIMITS
\par FIGURE OF MERIT REQUIRED= 100
\par MAX NUMBER OF UNINDEXED LINES IN FIGURE OF MERIT TEST= 1
\par THE 7 FIRST LINES ADJUSTED BY THEIR HIGHER ORDERS
\par CUBIC,TETRAGONAL,HEXAGONAL AND ORTHOROMBIC SYMMETRY
\par MAX CELL EDGE= 25.0 MAX CELL VOLUME= 2000.0
\par D1= .000200 SSQTL= .050000 D2= .000400 WAVE= 1.540598
\par NUMBER OF TEST LINES= 5 IQ REQUIRED= 2
\par
\par \plain\f3\fs20\cf1 ** CUBIC TEST **********\plain\f3\fs20\cf0
\par MAX. VOLUME= 2000.
\par SELECTED BASE LINES (1) (2)
\par BASE LINE ONE.(HKL)-MAX= 4 4 4 MAX H+K+L= 0
\par
\par \plain\f3\fs20\cf1 ** TETRAGONAL TEST **********\plain\f3\fs20\cf0
\par MAX. VOLUME= 2000.
\par SELECTED BASE LINES (1,2) (1,3) (2,3)
\par BASE LINE ONE.(HKL)-MAX= 4 4 4 MAX H+K+L= 4
\par BASE LINE TWO.(HKL)-MAX= 4 4 4 MAX H+K+L= 4
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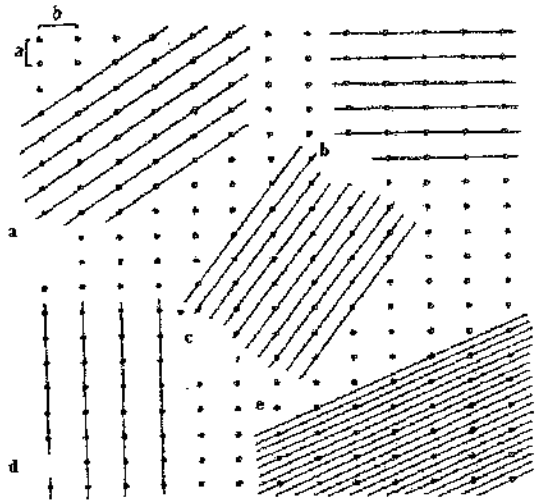
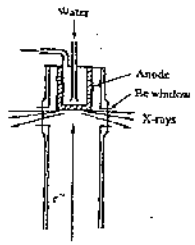
The following figures show experimental x-ray diffraction patterns of cubic SiC using X-ray synchrotron radiation.

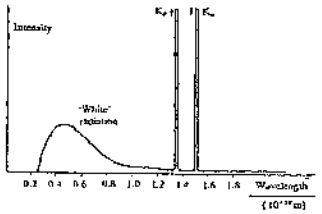
1.Give Miller indices to following planes:



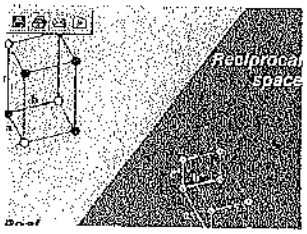
2. How is X-ray produced?



3. What are K_α and K_β lines how are they separated to get monochromated radiation?



4. What's real space and reciprocal space in X-ray crystallography? How is it different from each other?

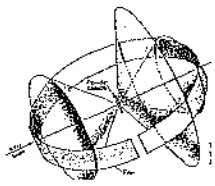


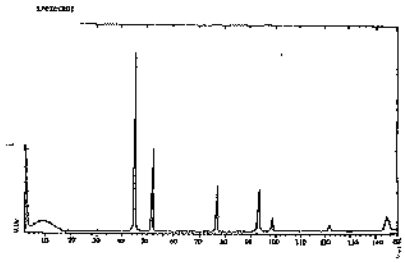
5. How you get the cubic cell dimensions from its reciprocal cell dimensions?

6. Obtain a powder diffraction pattern for NaCl and compare it with the one you calculated in the previous lab.

7. Index the powder diffraction pattern for NaCl and compare it with the indexing you calculated last week.

8. Describe how Debye-Scherrer powder diffraction is related to modern CPS vs. 2θ plots.





9. A Debye-Scherrer powder diffraction experiment using incident copper Kα raditation (λ, of 1.5418 Å) gave the following set of reflections expressed as 2θ: 38.40°; 44.50°; 64.85°; 77.90°; 81.85°; 98.40°; 111.20°.

$$\sin^2\theta = \frac{\lambda}{4a^2}(h^2+k^2+l^2)$$

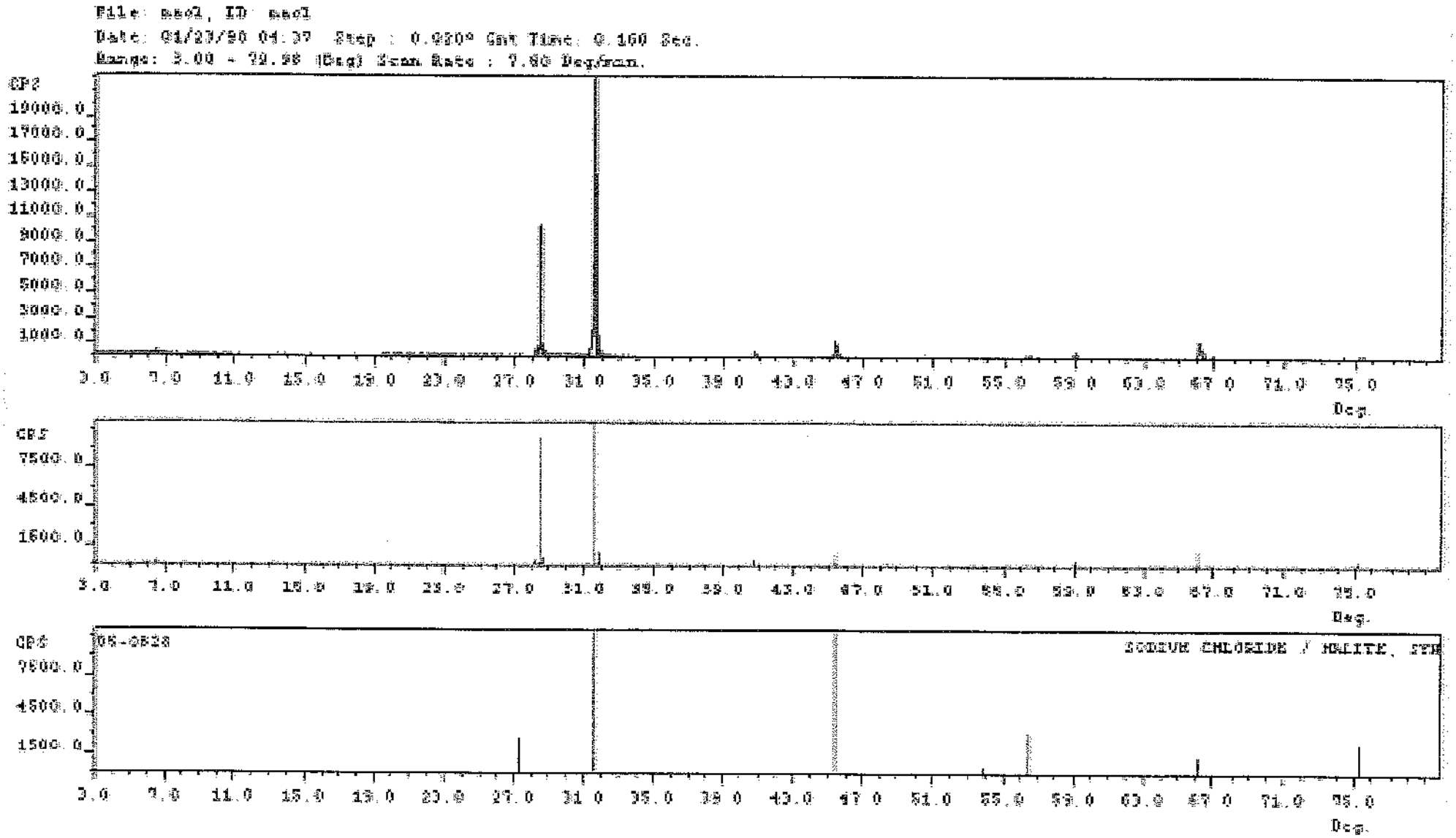
Now assign whole numbers

λ = 1.54 Angstroms W = 180mm

S_1 (mm)	θ	$\sin^2\theta$	$K\sin^2\theta$	$h^2+k^2+l^2$	hkl	a(Å)
38	19.0	0.11	3.0	3	111	4.05
45	22.5	0.15	4.1	4	200	4.02
66	33.0	0.30	8.2	8	220	4.02
78	39.0	0.40	10.9	11	311	4.04
83	41.5	0.45	12.3	12	222	4.02
97	49.5	0.59	15.8	16	400	4.04
113	56.5	0.70	19.1	19	331	4.03
118	59.0	0.73	19.9	20	420	4.04
139	69.5	0.88	24.0	24	422	4.01
168	84.0	0.99	27.0	27	511	4.03

Multiply by 27.3 in this case

θ	$\sin^2\theta$	$K\sin^2\theta$	$h^2+k^2+l^2$	hkl


File: nacl, ID: nacl
Date: 01/23/90 04:37 Step : 0.030° Cnt Time: 0.160 Sec.
Range: 3.00 - 79.98 (Deg) Scan Rate : 7.80 Deg/min.
CPS
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