CHAPTER I

GENERAL INTRODUCTION

I.1   INTRODUCTION TO THE PHASE PROBLEM

The importance of structure determination for understanding physical and chemical properties of materials as well as for manufacturing compounds of medical, industrial and agricultural interest is now well established. X-ray diffraction is best suited for the purpose of structure determination since the wavelength of X-rays is of the same order as the interatomic distances making it suitable for resolving small objects of atomic dimensions. Electron and Neutron beams have associated De Broglie Waves of the same order of magnitudes. However, neutron diffraction involves the problem of instrumental difficulties, whereas electron diffraction can give informations mainly about surface structures only. All these three techniques together yield the correct structure - but X-ray studies are most important because of ease of instrumentation and wealth of information yielded. Direct photography of atoms with X-rays is not possible, since X-ray lenses cannot be constructed because of the fact that refractive index of X-rays for all substances is very nearly equal to unity. Hence only diffraction patterns can be obtained experimentally from which the atomic positions are to be inferred. Interpretation of diffraction pattern of crystalline substances is relatively easier than those of amorphous substances and same is true for single crystals in comparison to polycrystalline materials. Thus

single crystals can yield best possible informations about
the structure of a substance.

The diffraction of X-rays from crystals gives rise
to distinct spots which can be recorded photographically.
The intensity of a spot in the direction (h k l) is given
by

$$I_{hkl} = F_{hkl} \; F^*_{hkl} \tag{1.1}$$

where $F_{hkl} = \left| F_{hkl} \right| e^{i\phi_{hkl}}$

and

$$F^*_{hkl} = \left| F_{hkl} \right| e^{-i\phi_{hkl}} \tag{1.2}$$

ϕ_{hkl} being the phase angle of the diffracted wave.
F_{hkl}, the structure factor of the reflection (hkl) is
given by

$$F_{hkl} = \int_V \rho(x,y,z) \exp 2\pi i \, (hx + ky + lz) \, dv \tag{1.3}$$

where $\rho(x,y,z)$ is the electron density, at the point
(x,y,z).

F_{hkl} and $\rho(x,y,z)$ are Fourier transform of each other,
the electron density at any point (x,y,z) being given by

$$\rho(x,y,z) = \frac{1}{V} \sum_{h} \sum_{k}^{\infty} \sum_{l} F_{hkl} \exp\left[-2\pi\, i(hx + ky + lz)\right]$$

$$(1.4)$$

If F_{hkl} is known, $\rho(x,y,z)$ can be calculated and the
peaks in an electron density plot can give the positions of
the atoms. But it is the intensities of reflections that
are experimental observables and because $I_{hkl} = |F_{hkl}|^2$,
only amplitudes of structure factors can be obtained from
intensities, whereas the information regarding phase cannot
be derived directly from the intensities. This lack of
information regarding phases gives rise to difficulties and
ambiguities in the unique interpretation of diffraction
patterns in terms of location of atoms in the unit cell.
Similar problems exist in optics and electronics where the
solution is easier because of ancilliary informations
available in these cases. For interpretation of X-ray
diffraction patterns from crystals, such ancilliary infor-
mations are not available. Hence the problem is most
difficult in this case. A large amount of work has been
carried out to solve this problem by many eminent and not
so eminent scientists and a huge literature has grown on
this problem. In what follows, a brief account of the most
important steps taken and achievements made has been given.