CHAPTER - I

INTRODUCTION

1.1 Introductory remarks :

Materials occur in three states of aggregation : solid, liquid and gaseous. In solids and liquids the distance between the neighbouring atoms is of the order of a few Angstroms i.e., they contain about $10^{22} - 10^{23}$ atoms per cm^3. This may be compared with a density of about 2.7×10^{19} molecules per cm^3 in a gas at room temperature and a pressure of one atmosphere. This corresponds to an average distance of approximately $30\overset{o}{A}$ between molecules.

Depending on external morphology and internal atomic arrangements, solid materials can be broadly divided into two groups - amorphous and crystalline with various shades of crystallinity lying in between. An ideal crystal is defined to consist of atoms stacked in a regular manner, forming a three dimensional array, which may be obtained by a three dimensional repetition of a certain pattern unit. A perfect crystal should also be infinite in size since finiteness of size means break of regularity of atomic arrangements at the boundary. Atoms in a perfect crystal must necessarily be stationary at lattice points. These conditions of an ideal crystal are obviously not realizable in practice. All real crystals are finite in size and even a

so called single crystal consists in reality, of small crysta-
llites called domains or mosaic blocs misoriented among them-
selves by small finite angles. At all temperatures - even at
absolute zero - the atoms in a crystalline. solid execute small
oscillations about their mean equilibrium position. Apart from
this, there may be displacements of the mean positions from the
lattice site, caused by dislocations, strain, stacking and
twining faults and also by introduction of foreign atoms. There
may be vacancies and interstitials and sometimes cracks and voids.
The periodicity of the lattice is broken due to presence of
these defects. A more serious type of defect is the lattice
disorder where different constituent atoms randomly occupy the
lattice sites.

For most solids the crystalline state is the natural one
since the energy of the ordered atomic arrangement is lower than
that of an irregular packing of atoms. However, when the atoms
are not given an opportunity to arrange themselves properly,
mostly natural but sometime man-made amorphous materials may be
formed. The ideal amorphous material is one in which atoms are
distributed with perfect randomness. It is easy to see that
such perfect amorphous materials are very difficult to obtain
specially when the finite size of the atoms produces a local
regularity of arrangements. An amorphous material is found to
possess a short range order in the sense that over the range of
3 to 5 atomic diameters the atomic arrangement is largely repe-
titive. Macroscopically speaking amorphous substances are

necessarily isotropic so that their bulk properties do not vary
with direction.

In liquids and gases, the atomic environment about any
reference atom is constantly changing. Nevertheless, a small
degree of local order prevails in liquids. This is demanded by
the hard sphere model of atom - which prohibits atoms and
molecules approaching each other beyond a certain distance known
as radius of the sphere of influence. Additional nearly constant
interatomic distances are introduced which are determined by the
lengths of the bonds and any characteristic angle between them.
Certain polymers are composed of very large and irregular mole-
cules and in such cases, closed packing may not be observed and
isotropy will mostly disappear.

Since early times, exponents of science have carried out
extensive researches on crystals and many new horizons in this
particular branch of science have been explored. Of late,
amorphous materials especially amorphous semiconductors have
attracted attention of the scientists all over the world and many
fascinating properties of these materials have been studied. This
rapidly growing field of physics has now become a very important
branch of crystallography.

Because of the many uses to which it is increasingly
being put - for example as monochromator for X-rays and neutrons,
as replica material for electron microscopic studies, for slowing
neutrons in nuclear reactors, as electrode materials, in the

manufacture of rocket nozzles as rubber hardeners etc., carbon
is being studied recently from many standpoints. The most
important and fascinating aspects are obviously the structure-
property relations. Admittedly, the present investigation has
been necessiated from this consideration and as such, different
samples of carbons especially of amorphous type have been taken
up for detailed X-ray analysis.

The tool for structural studies of carbon has been
chosen to be the X-ray diffraction technique. The arrangement of
atoms can be studied by using radiations with wavelength of the
order of interatomic distances i.e., of the order of 1A.U.
Usual radiations having this order of wavelengths are X-rays,
electron beams and neutron beams. A combination of studies
using all of these three radiations would be very useful but
X-rays are most easily available and for wide angle studies, very
elegant. The same angular range can be covered by Neutron
diffraction studies - but neutron beams of required intensity
can be obtained only from Nuclear reactors which are not easily
available. The associated instrumentation is also very compli-
cated. Electron microscopy and electron diffraction are both
useful tools and have been used quite often for studying carbon
structures. But the effective resolution of usually available
electron microscope is of the order of at most 100 A.U. although
claims for special instruments with higher resolution have been
made. Electron beams of wavelength of the order of X-rays
(1 A.U.) present problems of penetrability and high refractive

index caused by potential barrier due to atoms. Shorter wave-
lengths used to avoid these difficulties give rise to very small
angles of diffraction. The measurements in this angular range
become rather inaccurate. Thus, on an overall basis, X-rays are
the most convenient radiations to use - although electron
diffraction and neutron diffraction provide very valuable comple-
mentary data. For X-rays, the refractive index being very near
to unity, it is not possible to construct lenses for X-rays thus
rendering construction of X-ray microscope a very difficult task.
So we are left with X-ray diffraction and it is this technique
that has been used in course of this analysis.

In the first phase of the present dissertations, carbon
blacks obtained from pyrolysis of analytically pure benzene,
toluene and socrose and also a sample of ultracarbon have been
subjected to extensive X-ray study with special emphasis to
examine whether the mother substance has any influence on the
residual amorphous carbon black. In the second phase, a syste-
matic study has been made on the nature and extent of graphiti-
sation of a few cokes and graphites prepared from naturally
occurring coals.

1.2 Dependence of properties of carbon on structure :

The element carbon is the sixth in the periodic table.
Of the six electrons in a neutral atom, the four in the outer
L-shell are available for the formation of chemical bonds. In
the isolated carbon atom the distribution is $1s^2 2s^2 2p^2$,