Structural Characterization

X-ray Diffraction Technique

X-ray Diffraction (XRD) is one of the classical methods for identification and characterization of crystalline solids. Each crystalline solid has its unique characteristic X-ray powder pattern which is used as a" fingerprint" for its identification. The method is based on the diffraction of X-rays by the sample in different directions. Waves of wavelength comparable to the crystal lattice spacing are strongly scattered (diffracted). The X-ray source is Cu X-ray having a wavelength of Cu *Ka* lines, 1.54 °A The diffracted rays are detected by a detector placed on the opposite side shown in figure .The X-ray source, sample and the detector are placed in a particular configuration given by the Bragg-Brentano geometry that gives a θ-2θ scan. The source is stationary and the sample and the detector are mobile. When the sample moves by an angle θ, the detector moves by angle 2θ. The rotation rate is kept at 1°/min and the sample is scanned for 10°-80° scan.

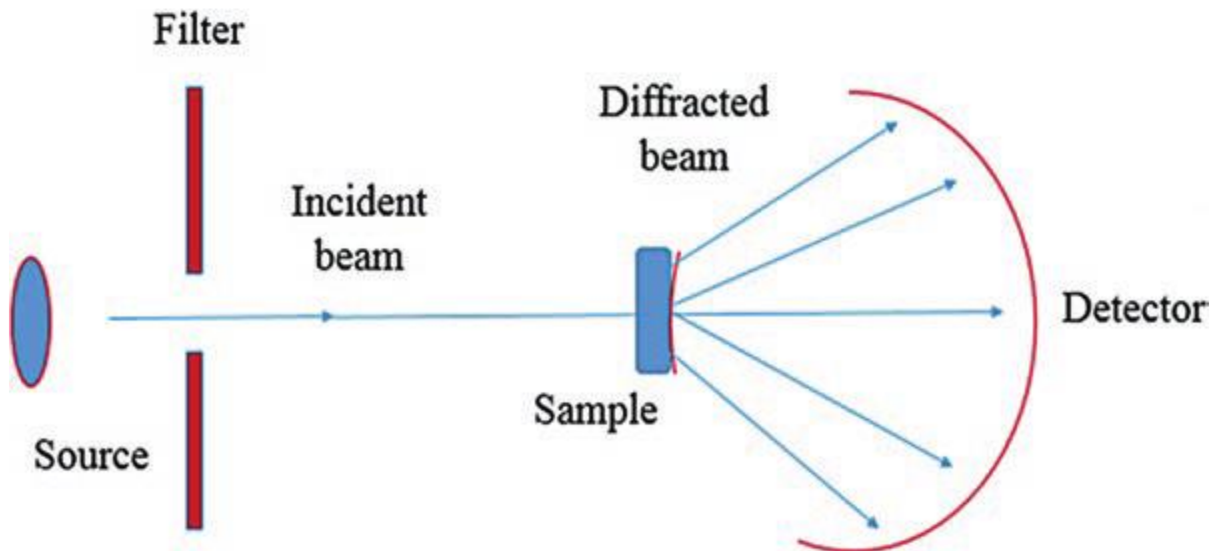

Fig. A schematic of X-Ray diffractometer

The angle and intensities of the diffracted X-rays are used to perform crystallographic studies.

The intensity of the diffracted X-rays is measured as a function of the diffraction angle 2θ .The intensities of the peak provides information about the atomic basis. The sharpness and shape of the peak are related to the perfection of the crystal.

The structural information of the material can be obtained from intensity Vs 2θ plot

(i) The presence or absence of a certain sets of peaks corresponding to different planes gives us the crystal structures.

(ii) The shift of the peaks from its original positions in case of bulk crystals gives the strains in the material.

Although the method of X-ray diffraction is quantitative, in general,it is used for qualitative analysis. This form of analysis, extends to all crystalline solids including ceramics, metals, insulators, organic, polymers, thin film powders etc. X-ray diffractometers can be used either for single crystals or for powders. While single crystal diffractometers are used for the study of molecular structure, powder diffractometers are used for analysis of phases, though the latter can also be used to derive molecular information.

Diffraction from different type of Material

So far we considered the diffraction from a set of planes, assuming them to be infinite in number. We may have samples which are single crystalline, polycrystalline solids, liquids or even gases. Amorphous solids, liquids, gases and nanocrystalline materials do not have infinite ordered arrangement of atoms but have few atoms and few planes (small single crystals or crystalline nanomaterials). Nanoparticles with disordered structure can be treated like amorphous bulk solids. In Fig. the differences in scattering of X-rays by different materials are shown. It can be seen that in case of a monoatomic gas (like He, Ar, Kr etc.) forward scattering occurs without any diffraction peaks in any other direction. In case of liquids or amorphous solids one or two peaks at angles other than the angle of incidence appear due to short range order in these materials. For single crystals, diffraction peaks appear at various angles. Intensities of peaks depend upon atomic scattering factor as well as crystal structure (or form) factor which we shall consider in the following section. The diffraction peaks from ideal single crystals are sharp, and broadened to certain extent only by instrumentation factor. However in case of polycrystalline sample the peaks are broadened due to the size of the grains. All the grains in crystal may not be of the same size. Therefore the width of the diffraction peaks can be considered as the effect of

convolution of different peaks giving the average grain size. The diffraction peaks are broadened in case of nanoparticles also due to small number of atoms and planes present in them. We shall discuss this in a following section and show how one can determine the average particle size using the widths of diffraction peaks.

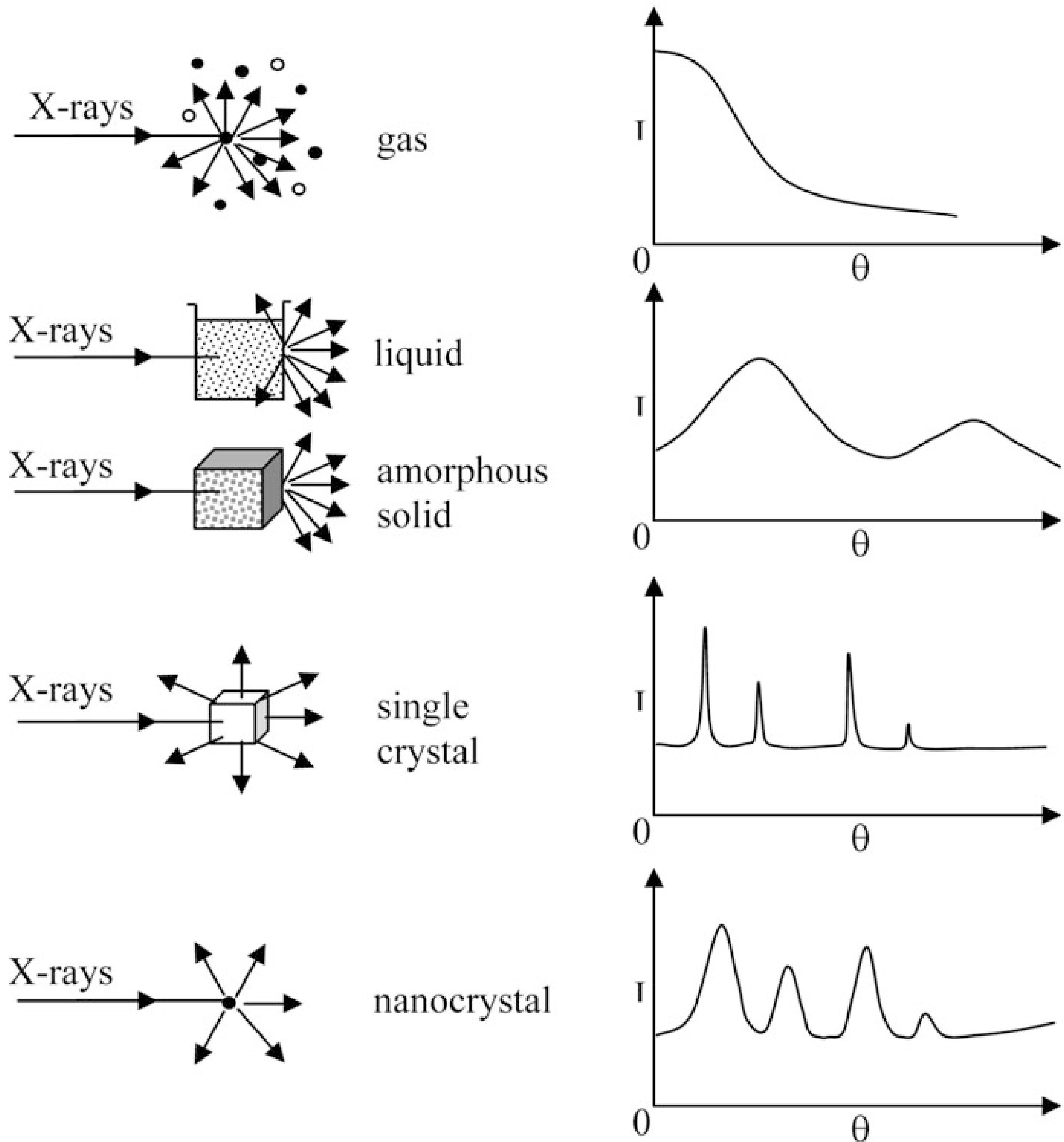

Fig. Diffraction from the gas liquid solid and nanocrystal

Diffraction from Nanoparticles (Scherrer equation)

We know that in a nanoparticle number of atoms is very small. Nanoparticles cannot be considered as an infinite arrangement of atoms as is usually assumed in Solid State Physics, in order to determine various properties of solids. In case of amorphous nanoparticles, similar to an amorphous bulk solid material, broad diffraction peaks are expected to occur. However in case of nanoparticles in which atoms do have ordered lattices some changes in diffraction are to be expected as compared to single crystal or polycrystalline bulk solid diffraction (often the nanoparticles are similar to single crystals and do not have grain boundaries). It has been found that the diffraction peaks in nanocrystalline particles are broadened compared to single or polycrystalline solid of the same material.

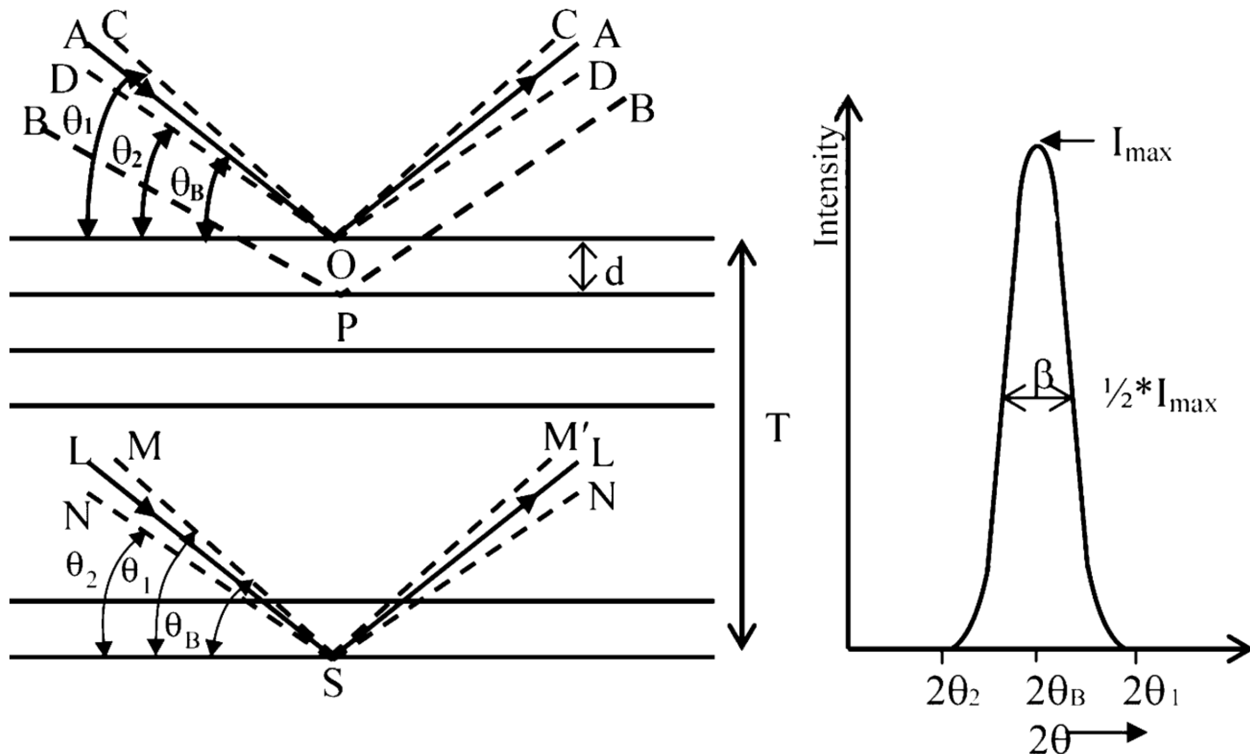

Fig. Effect of particle size on the X-ray diffraction

Consider a limited number of planes say 0,1,……. m or total m+1 planes in a set. Let d_{hkl} be the interplaner distance. If the thickness of the crystal is say T then T = m d_{hkl}. The X-rays of a single wave length allow falling on the set of planes d_{khl}. All the rays in a beam may not be exactly parallel to each other. As shown in Fig. rays AO, BP, : : : , LS only are parallel and make

angle θ_B with parallel planes (hkl). Let these rays scatter coherently and interfere constructively to satisfy Bragg's diffraction condition. This should produce an extremely sharp peak widened only due to instrument limitation. However ray like CO is at slightly larger angle than θ_B and so is the ray MS striking the mth plane. Both CO and MS are parallel to each other. It can be understood that the ray like CO cannot interfere constructively with rays parallel to it just in 1st, 2nd etc. planes. But there would be a plane sa m at which it interferes constructively (Corresponding to thickness of crystal). Therefore

$$(m+1)\,\lambda = 2T \sin\theta_1 \ldots\ldots\ldots\ldots\ldots 1$$

And for any such as DO let the constructive interference occur just one plane before the mth plane, so

$$(m-1)\,\lambda = 2T \sin\theta_2 \ldots\ldots\ldots\ldots\ldots 2$$

Subtracting equation 2 from 1 we get

$$\lambda = T\,(\sin\theta_1 - \sin\theta_2)$$

Therefore

$$\lambda = 2T \cos\left(\frac{\theta 1+\theta 2}{2}\right) \sin\left(\frac{\theta 1-\theta 2}{2}\right)$$

$$\text{as} \quad \frac{\theta 1-\theta 2}{2} = \theta_{\mathbf{B}} \quad \text{and } \sin\left(\frac{\theta 1-\theta 2}{2}\right) = \left(\frac{\theta 1-\theta 2}{2}\right) = \frac{\beta}{2}$$

Thus we get

$$\lambda = 2T\,\frac{\beta}{2}\,\cos\theta_B \quad \text{and} \quad T = \frac{\lambda}{\beta \cos \theta \boldsymbol{B}}$$

More correctly

$$T = \frac{0.9\,\lambda}{\beta \cos \theta \boldsymbol{B}}$$

This is known as Scherrer equation we can find out average particle size less than 100 nm .

References

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