EXPERIMENTAL MODULE 6

Determination of Crystallite Size and Lattice Strain

OBJECTIVE OF THE EXPERIMENT

To determine the average crystallite size and lattice strain in a powder specimen by x-ray peak broadening analysis.

MATERIALS REQUIRED

Copper metal powder obtained by filing a bulk copper specimen (effectively a cold-worked sample).

BACKGROUND AND THEORY

In deriving Bragg's law, we assume that ideal conditions are maintained during diffraction. These conditions are that the crystal is perfect and that the incident beam is composed of perfectly parallel and strictly monochromatic (single wavelength) radiation. These conditions never actually exist. In fact, only an infinite crystal is really perfect. Finite size alone, of an otherwise perfect crystal, can be considered a crystal imperfection.

The "ideal" size for powder diffraction depends on the relative perfection of the polycrystalline material, but is usually 500 nm (0.5 μm) to 10,000 nm (10 μm). If the crystallites are smaller, the number of parallel planes available is too small for a sharp diffraction maximum to build up, and the peaks in the diffraction pattern become broadened.

A crystal is usually considered perfect when all lattice sites are occupied by atoms and no imperfections (point: vacancies, interstitials; linear: dislocations; planar: grain boundaries, stacking faults; or volume: voids, precipitates) exist in the crystal. Crystals are never perfect in this sense because they contain varying amounts of defects under equilibrium conditions. For example, at room temperature, aluminum has an equilibrium vacancy concentration of 1.4×10^{-13}. The vacancy concentration in semiconductors and ceramics is generally much lower. Although dislocations are not equilibrium defects, they are present in most materials. A dislocation density of about 10^6 m/m^3 is typical for well-annealed metals at room temperature. In single-crystal silicon, made for integrated circuits, the dislocation density is approximately zero. In the present context, a perfect crystal is considered as one in which the interplanar spacings are uniform and there are no distortions in the planes.

Broadening of x-ray diffraction peaks is easily apparent in patterns obtained with a diffractometer, and this information can be directly quantified. However, it is important to realize that broadening of diffraction peaks arises mainly due to three factors.

1. *Instrumental effects*: These effects include imperfect focusing, unresolved α_1 and α_2 peaks, or the finite widths of the α_1 and α_2 peaks in cases where the peaks are resolved. These extraneous sources can cause broadening of the diffraction peaks. Thus, the ideal peak shape—a peak without any noticeable width (Fig. 6.1a)—gets transformed to that shown in Fig. 6.1b due to instrumental effects.

2. *Crystallite size*: The peaks become broader due to the effect of small crystallite sizes, and thus an analysis of peak broadening can be used to determine the crystallite sizes from 100 to 500 nm. Small crystallite sizes introduce additional broadening into the diffraction peaks; therefore, in the presence of instrumental effects, crystallite sizes broaden the peak as in Fig. 6.1c.

3. *Lattice strain*: If all the effects mentioned are simultaneously present in the specimen, the peak will be very broad, as shown in Fig. 6.1d. However, it is possible to separate the individual effects of broadening by following some simple procedures, which will now be described.

Some Definitions

Some terms you will come across in the literature on peak-broadening effects are *domain size*, *crystallite size*, and *grain size*. These terms have created

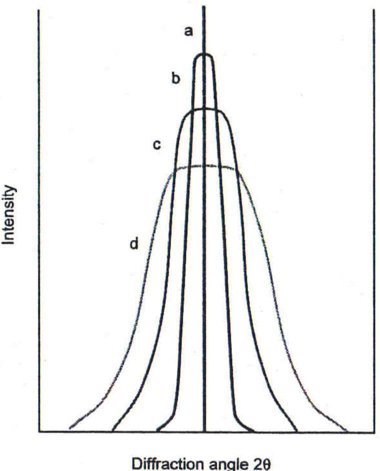

FIG. 6.1. X-ray diffraction peak widths: (a) ideal, (b) due to instrumental effects, (c) superimposition of instrumental and crystallite size effects, and (d) combined effects of instrumental, crystallite size, and lattice strain effects (not drawn to scale).

some confusion, so we will try to clarify their meanings. A domain is that part of the specimen that diffracts the x-ray beam coherently, and it is sometimes called a coherently diffracting domain. The domains form a substructure, which can occur in single crystals and in polycrystalline materials. The individual domains are very slightly misoriented (generally $< 1°$) with respect to each other, and they are smaller than the grain size of the material. For example, the grains may be divided by low-angle grain boundaries (a planar arrangement of individual dislocations). A cold-worked (and partially or fully recovered) metal, for example, has domains (referred to as subgrain boundaries or cells separated by low-angle grain boundaries). A well-annealed metal does not have domains (subgrain boundaries), but does have grains.

For completeness, we mention that faulting in crystals also affects the shape of the diffraction peaks. The effects are complex and depend on the crystal structure and nature of faulting. An excellent treatment of the topic can be found in B. E. Warren (*X-Ray Diffraction*, Addison-Wesley, Reading, MA, 1969, pp. 275–312). These effects will not be considered further in this module.

Recording x-ray diffraction patterns on photographic film in a camera (though not used now) is an ideal way to differentiate qualitatively between materials with coarse- and fine-sized crystallites. The x-ray diffraction patterns are in the form of a series of concentric rings. Each ring represents diffraction from a set of planes in the crystal. When the crystallites are larger than about 10 μm, the number of crystallites in the irradiated portion of the specimen is insufficient to reflect to each portion of the ring, and consequently the ring becomes spotty. Between 500 nm (0.5 μm) and 10,000 nm (10 μm), the number of crystallites is sufficient to produce a smooth and continuous ring pattern, and this is considered the "ideal" size of the crystallites. If the crystallite size is small, say 100 nm (0.1 μm) to 500 nm (0.5 μm), then the diffraction ring becomes broadened. However, if it is extremely small, say << 100 nm (0.1 μm), then the irradiated volume is too small to build up any diffraction ring and diffraction occurs only at low angles. Thus, by observing the diffraction rings in a series of powder patterns made from specimens containing different crystallite sizes, one can qualitatively grade the crystallite sizes in a particular order. This is qualitatively similar to what happens in electron diffraction. The smaller the crystallite size the more broadened are the diffraction rings, and the larger the crystallite size the more spotty the diffraction rings. In fact, one can count the number of spots in a diffraction ring recorded under a given set of conditions (specimen condition, crystallite size, type and radius of camera, operating conditions of the x-ray diffraction unit, etc.) and use such data as standards. The crystallite size of an unknown specimen can then be determined by comparison with these standard patterns (such as ASTM grain size charts).

Crystallite is a more general term and may mean a domain with reference to, for example, a cold-worked (and partially annealed) metal or a grain in the case of a well-annealed metal. In the literature these terms are used interchangeably. In ionic or covalently bonded materials a domain structure is unlikely because the dislocation densities are generally much lower and dislocation movement is more difficult than in a metal. In a nanocrystalline material the grain size is so small (~10 to 100 nm) that it will not be possible to have a substructure, so crystallite, domain, and grain all mean the same thing.

The definitions of the terms we use in this module, peak height and FWHM (full width at half maximum) are indicated in a typical x-ray diffraction peak in Fig. 44 in Chapter 3 of Part I. The broadening is evaluated by measuring the width B, in radians, at an intensity equal to half the maximum intensity (FWHM). Note that B is an angular width, in terms of 2θ (not θ), and not a linear width.

Subtraction of Instrumental Broadening

The individual contributions of small crystallite sizes and lattice strains to the peak broadening can be determined only after first subtracting the effect of instrumental broadening from the experimentally observed peaks. In order to estimate the magnitude of instrumental broadening, it is usual to mix the unknown specimen with some coarse-grained, well-annealed (i.e., strain-free), standard powder whose crystallite size is so large that it does not cause any broadening. For example, silicon powder (a brittle material that can be produced in powder form with no stored lattice strain) with a grain size of about 10 μm is ideal for this purpose.

An x-ray diffraction pattern of the standard powder is recorded under instrumental conditions identical to those of the unknown specimen, so the peak broadening of the standard material due to instrumental effects is exactly the same as instrumental broadening in the diffraction pattern of the unknown specimen. We should take proper care to see that one or more of the x-ray peaks of the standard specimen lie close to (but do not overlap) reflections from the unknown specimen; this ensures that the instrumental broadening is measured at similar Bragg angles for both materials.

Alternatively, we can use a powder of the same composition, if possible, as the experimental material, but in an annealed condition so that the grain size is large and the lattice strain is removed. This procedure has the added advantage that the peak width in the standard and experimental materials is measured at exactly the same angle.

If the observed x-ray peak has a width B_o, and the width due to instrumental effects is B_i, then the remaining width B_r is due to the combined effects of crystallite size and lattice strain:

$$B_r = B_0 - B_i \tag{6.1}$$

This expression is true only when the peak has a Lorentzian (Cauchy) profile. However, if it has a Gaussian profile, a better expression is

$$B_r^2 = B_0^2 - B_i^2 \tag{6.2}$$

In the absence of clear-cut evidence for the exact nature of the peak, we use the geometric mean to get a more nearly correct expression:

$$B_r = \sqrt{(B_0 - B_i)}\,\sqrt{(B_0^2 - B_i^2)} \tag{6.3}$$

In our analysis, however, we will use Eq. (6.2) to subtract the instrumental broadening from the observed broadening.

Most modern x-ray diffractometers include software for peak profile fitting. This software greatly helps in calculating the intensities, positions, widths, and shapes of the peaks with a far greater precision than is possible with manual measurements or visual inspection of the experimental data.

To apply the proper correction for the instrumental broadening, we must first decide the shape of the peak. The two most commonly assumed line shapes are the Lorentzian (Cauchy) and Gaussian. Even though exact mathematical descriptions can be provided for these two shapes, it is sufficient for us to realize that the most obvious difference between these two is the rate of decay of the tails. Figure 6.2 shows the computer-generated symmetrical Lorentzian (Cauchy) and Gaussian profiles with equal peak heights, 2θ, and FWHM. Note that the tails decay very fast for a Gaussian profile and more slowly for a Lorentzian profile.

Broadening due to Small Crystallite Size

Scherrer has derived an expression for broadening of x-ray diffraction peaks due only to small crystallite sizes:

$$B_{\text{crystallite}} = \frac{k\lambda}{L \cos\theta} \tag{6.4}$$

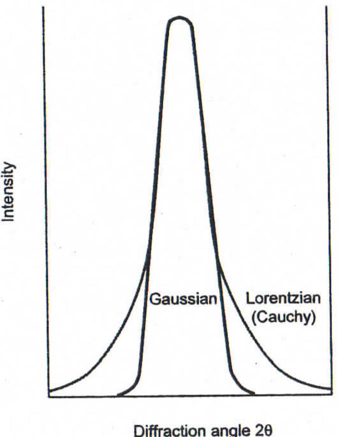

FIG. 6.2. Comparison of symmetrical Lorentzian (Cauchy) and Gaussian x-ray diffraction peak profiles.

where λ is the wavelength of the x-rays used, θ is the Bragg angle, L is the "average" crystallite size measured in a direction perpendicular to the surface of the specimen, and k is a constant. Equation (6.4) is commonly known as the Scherrer equation and was derived based on the assumptions of Gaussian line profiles and small cubic crystals of uniform size (for which $k = 0.94$). However, this equation is now frequently used to estimate the crystallite sizes of both cubic and noncubic materials. The constant k in Eq. (6.4) has been determined to vary between 0.89 and 1.39, but is usually taken as close to unity. Since the precision of crystallite-size analysis by this method is, at best, about ±10%, the assumption that $k = 1.0$ is generally justifiable.

Broadening due to Strain

The lattice strain in the material also causes broadening of the diffraction peaks, which can be represented by the relationship

$$B_{\text{strain}} = \eta \tan\theta \tag{6.5}$$

where η is the strain in the material.

From Eqs. (6.4) and (6.5) it is clear that peak broadening due to crystallite size and lattice strain increases rapidly with increasing θ, but the separation between these two is clearer at smaller θ values, as shown in Fig. 6.3. Since materials may contain both small crystallite sizes and lattice strains, it is desirable to use peaks at smaller diffraction angles to separate these two effects. (Remember that we used high-angle peaks for precise lattice parameter determination.)

The width, B_r, of the diffraction peak after subtracting the instrumental effect can now be considered as the sum of widths due to small crystallite sizes and lattice strains:

$$B_r = B_{\text{crystallite}} + B_{\text{strain}} \tag{6.6}$$

and from Eqs. (6.4) and (6.5) we get

$$B_r = \frac{k\lambda}{L \cos\theta} + \eta \tan\theta \tag{6.7}$$

Multiplying Eq. (6.7) by cos θ, we get

$$B_r \cos\theta = \frac{k\lambda}{L} + \eta \sin\theta \tag{6.8}$$

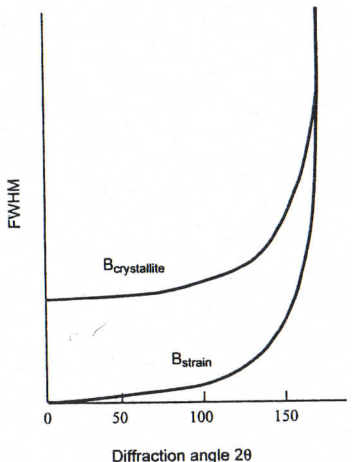

FIG. 6.3. Dependence of FWHM caused by crystallite size and lattice strain on the diffraction angle. Even though both widths increase rapidly with diffraction angle, the separation between them is large at small diffraction angles.

Thus, it is clear that when we plot $B_r \cos\theta$ against $\sin\theta$ we get a straight line with slope η and intercept $k\lambda/L$, as in Fig. 6.4a. The crystallite size L can be calculated from the intercept by using the appropriate values of k (generally taken to be = 1.0) and λ.

Equation (6.8) suggests that the larger the intercept the smaller the size of the crystallites and that for a sufficiently large crystallite size (which does not produce broadening of the diffraction peak), the straight line passes through the origin. The smaller the value of η, i.e., the flatter the straight line, the lower is the amount of strain in the material. These variations are shown schematically in Fig. 6.4b.

Most modern diffractometers have software supplied with the instrument to calculate crystallite sizes and lattice strains in materials. These programs can be used for this purpose. However, we advise you to do the calculations according to the foregoing procedures to be sure you understand them and their physical significance.

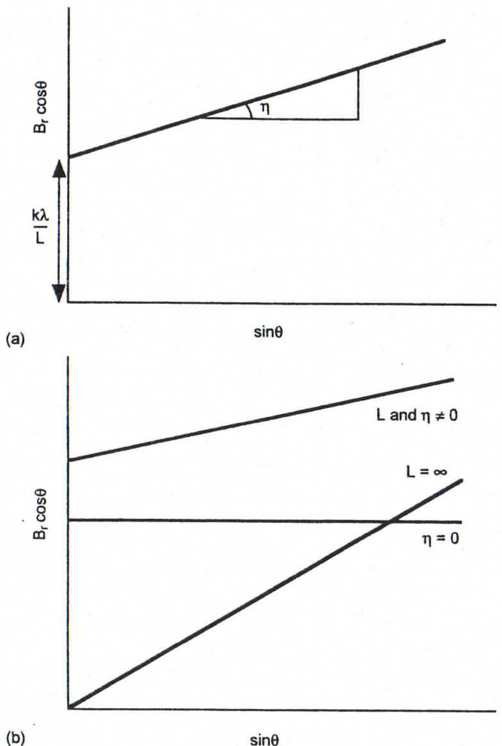

FIG. 6.4. (a) Plot of $B_r \cos\theta$ against $\sin\theta$, indicating that the intercept ($k\lambda/L$) and slope (η) can be used to calculate the crystallite size (L) and lattice strain (η), respectively. (b) Typical plots to show the relative positions of the straight line for very large crystallite sizes ($L = \infty$), no strain ($\eta = 0$), and when both lattice strain and crystallite size contribute to peak broadening.

WORKED EXAMPLE

Let's now work out an example to show how the crystallite size and lattice strain in a material can be calculated from the foregoing procedure. Aluminum metal powder was obtained by filing a bulk specimen; i.e., it is effectively a cold-worked specimen. An x-ray diffraction pattern of this specimen was recorded with Cu Kα radiation in the 2θ angular range of 30 to 70° and is presented in Fig. 6.5. For comparison purposes and to

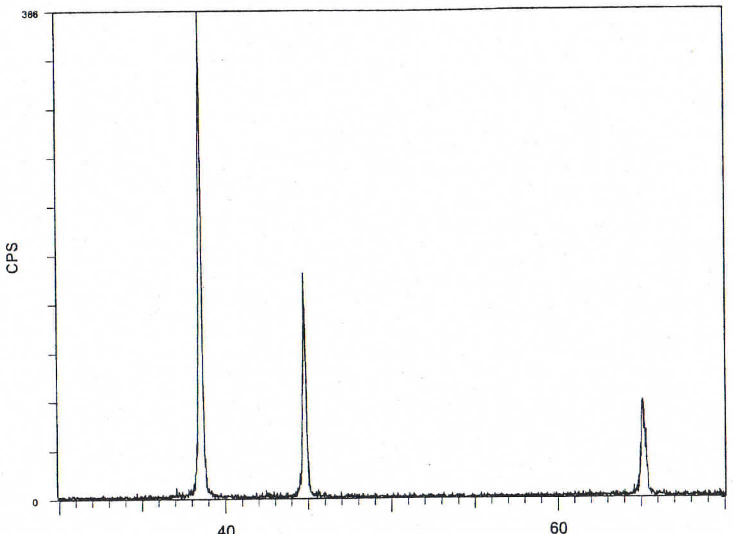

FIG. 6.5. X-ray diffraction pattern of cold-worked aluminum.

calculate the instrumental broadening, the diffraction pattern of an annealed aluminum specimen is presented in Fig. 6.6. Note that there are three peaks in this angular range. In Experimental Module 1, this pattern was indexed, and we found that these three reflections have indices 111, 200, and 220 at the 2θ values of 38.52, 44.76, and 65.13°, respectively. From the x-ray diffraction pattern of annealed aluminum (Fig. 6.6), the instrumental broadening B_i was calculated as the FWHM for the three

TABLE 6.1. Full-Width at Half-Maxima of Annealed Aluminum Specimen

Material: Annealed aluminum		Radiation: Cu Kα		λ = 0.154056 nm
Peak #	2θ (°)	*hkl*	FWHM (°)	FWHM (rad) = B_i
1	38.52	111	0.103	1.8×10^{-3}
2	44.76	200	0.066	1.2×10^{-3}
3	65.13	220	0.089	1.6×10^{-3}

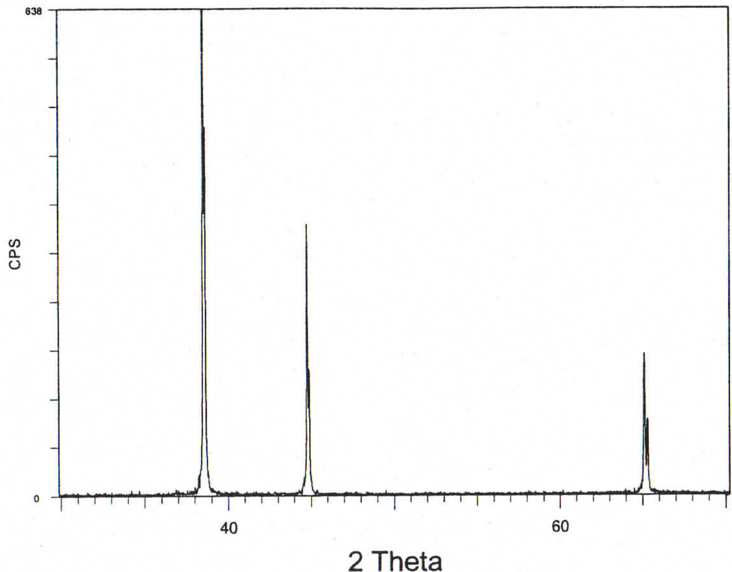

FIG. 6.6. X-ray diffraction pattern of annealed aluminum.

reflections. These calculations (measuring the width of the reflections B_0) were repeated for the experimental pattern recorded from the cold-worked aluminum sample. The remaining broadening was obtained by subtracting the instrumental broadening B_i from the observed broadening B_0, using Eq. (6.2). The results are tabulated in Tables 6.1 and 6.2.

A graph is now plotted between $B_r \cos\theta$ on the *y* axis and $\sin\theta$ on the *x* axis (Fig. 6.7). From the slope of this straight line the strain is calculated as 3.5×10^{-3}, and from the intercept the crystallite size is calculated as 90 nm.

TABLE 6.2. Calculations for Cold-Worked Aluminum Specimen

Material: Cold-worked aluminum			Radiation: Cu Kα			λ = 0.154056 nm	
Peak #	2θ (°)	sin θ	*hkl*	B_0 (°)	B_0 (rad)	$B_r^2 = B_0^2 - B_i^2$	$B_r \cos\theta$
1	38.51	0.3298	111	0.187	3.3×10^{-3}	2.8×10^{-3}	2.6×10^{-3}
2	44.77	0.3808	200	0.206	3.6×10^{-3}	3.4×10^{-3}	3.1×10^{-3}
3	65.15	0.5384	220	0.271	4.7×10^{-3}	4.4×10^{-3}	3.7×10^{-3}

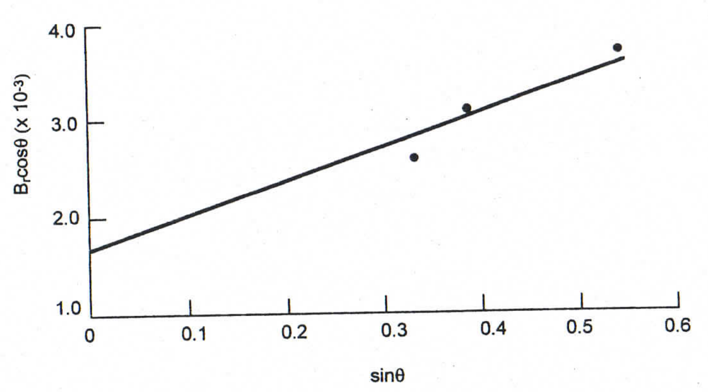

FIG. 6.7. Plot of $B_r \cos \theta$ versus $\sin \theta$ for cold-worked aluminum.

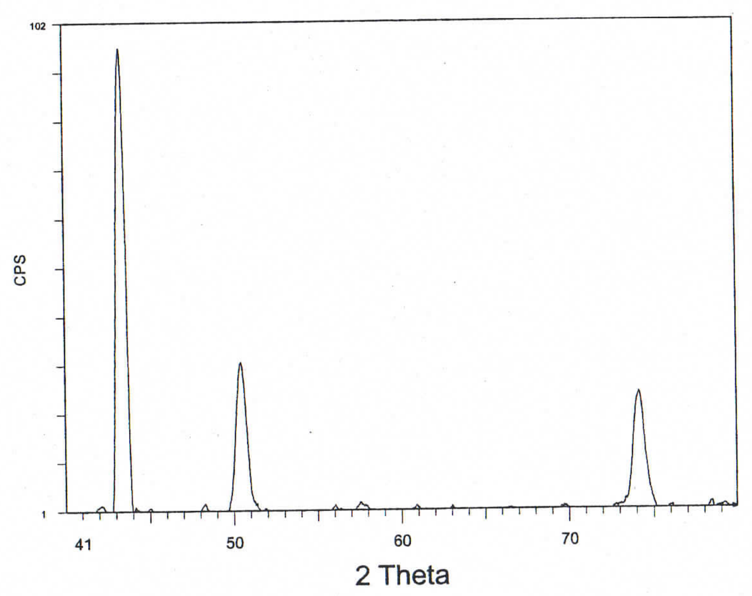

FIG. 6.8. X-ray diffraction pattern of cold-worked copper.

EXPERIMENTAL PROCEDURE

Record the x-ray diffraction pattern from a heavily-cold-worked copper powder, using Cu Kα radiation in the angular range of 2θ from 40 to 80°. Identify the *hkl* values of the different peaks based on your earlier indexing of this pattern in Experimental Module 1. Measure the FWHM for all the peaks. (Remember that the widths are in 2θ angular measure and you should express them in radians.) Evaluate the peak broadening due to instrumental effects, using a well-annealed copper specimen. Subtract this instrumental peak width from the observed peak widths of copper, and determine the crystallite size and lattice strain from all the reflections in the pattern. We have provided x-ray diffraction patterns of a heavily-cold-worked copper powder (Fig. 6.8) and a well-annealed copper powder (Fig. 6.9) if you are not able to record the diffraction patterns yourself.

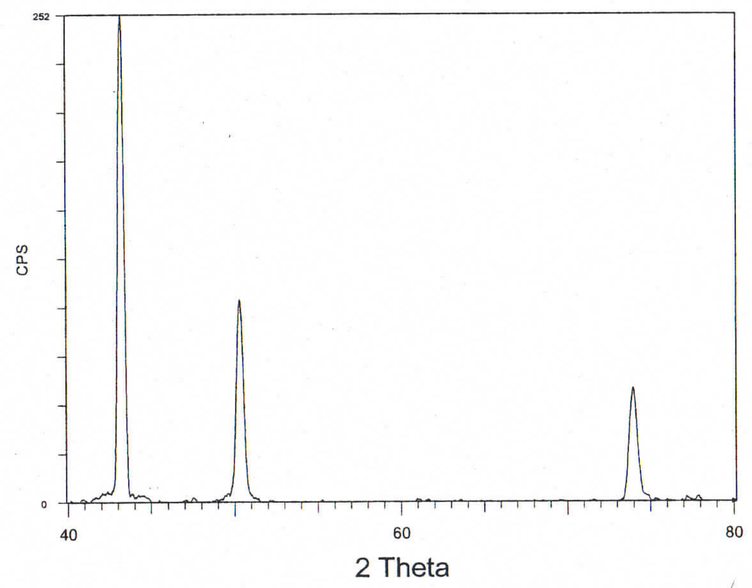

FIG. 6.9. X-ray diffraction pattern of annealed copper.

TABLE 6.3. Work Table for Annealed Copper Specimen

Material: Annealed copper Radiation: Cu Kα $\lambda = 0.154056$ nm

Peak #	2θ (°)	*hkl*	FWHM (°)	FWHM (rad) = B_i
1	43.16	111	0.260	
2	50.30	200	0.330	
3	73.99	220	0.438	

TABLE 6.4. Work Table for Cold-Worked Copper Specimen

Material: Cold-worked copper Radiation: Cu Kα $\lambda = 0.154056$ nm

Peak #	2θ (°)	sin θ	*hkl*	B_0 (°)	B_0 (rad)	$B_r^2 = B_0^2 - B_i^2$	$B_r \cos\theta$
1	43.31		111	0.465			
2	50.40		200	0.541			
3	74.19		220	0.676			

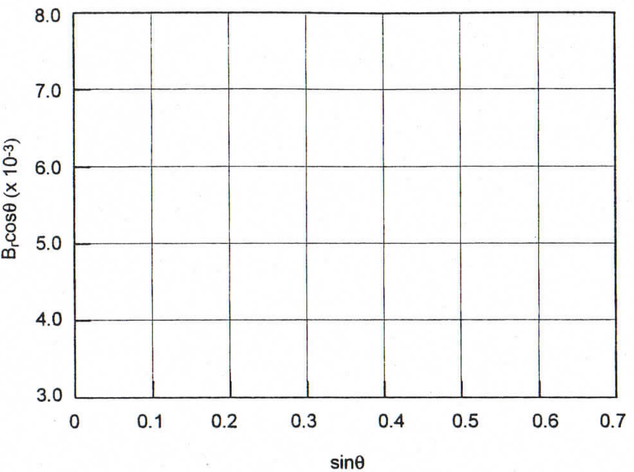

FIG. 6.10. Plot of $B_r \cos\theta$ versus $\sin\theta$ for cold-worked copper.

RESULTS

Tabulate your measurements in Table 6.3.

Further calculations can be done as shown in Table 6.4.

Now plot a graph with $B_r \cos\theta$ on the *y* axis and $\sin\theta$ on the *x* axis (Fig. 6.10). The slope of this straight line will be the strain (η), and the intercept is $k\lambda/L$, from which the crystallite size (L) can be estimated. Thus, in the cold-worked copper sample, the crystallite size is _____nm, and the strain is _____.

EXERCISE

6.1. Assume that x-ray diffraction patterns were recorded from an MgO specimen containing crystallites with a diameter of 100, 80, 60, or 40 nm. Calculate the width B (in degrees 2θ) due to the small crystal size alone, assuming that $\theta = 40°$ and $\lambda = 0.154$ nm. For 60-nm-diameter particles, calculate B for $\theta = 20, 40,$ and $60°$.