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The Refractive-Index Correction in Powder Diffraction

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Abstract

Throughout the history of powder diffraction practice there has been uncertainty about whether or not a refractive-index correction should be made to Bragg's law. High-precision Bragg-angle measurements have been performed with synchrotron radiation on SRM-640 silicon powders at glancing angles; it is found that little or no correction is necessary for the usual 2θ angle range.

1. Introduction

The question of the need to use a refractive-index correction for powder diffraction data has long been cloaked in uncertainty. The problem is discussed in this paper and is based on the theoretical background and recent measurements of a silicon-powder standard using synchrotron in high-resolution parallel-beam geometry.

When X-rays enter a material refraction at the surface causes a small shift of the observed Bragg reflection angles to larger 2θ values than indicated by Bragg's law. The shifts are normally much smaller than other sources of errors and corrections are not generally applied in the usual routine qualitative and quantitative powder diffraction analyses. The correction has been used mainly in precision lattice-parameter determination (*e.g.* Lipson & Wilson, 1941) but there is no general agreement, and some authors use it while others ignore it. In the 1960 IUCr round-robin test on the precision of lattice-parameter determination of powder samples with Cu $K\alpha$ radiation, the following values were added to the derived lattice parameters to correct for refraction: diamond 0·00004, silicon 0·00004 and tungsten 0·00016 Å (Parrish, 1960).

Synchrotron-radiation sources now provide improved resolution because high intensity and the narrow instrument functions can be simultaneously exploited (Hastings, Thomlinson & Cox, 1984; Parrish, Hart & Huang, 1986). The narrow symmetrical profiles and general absence of systematic errors open the possibility of higher precision and more reliable lattice-parameter determination (Parrish, Hart, Huang & Bellotto, 1987). The question of how one should correct powder data for X-ray refraction therefore becomes more important than it has been, especially because the move to synchrotron-radiation sources also means that wavelengths other than the 'standard' copper $K\alpha$ will be used.

In the growing field of grazing-incidence diffraction studies of thin films, the angular shifts are much larger than in conventional θ-2θ scanning and corrections are necessary for many of the analyses. This is described separately (Lim, Parrish, Ortiz, Bellotto & Hart, 1987).

2. Theoretical background

The index of refraction n of X-rays is slightly less than unity and is given by

$$n = 1 - \delta$$

where

$$\delta = (-e^2/2\pi mc^2)\lambda^2\rho; \qquad (1)$$

e is the charge on the electron, m is the electron mass, c is the velocity of light, λ is the wavelength in ångströms, and ρ is the number of electrons per unit volume. For wavelengths below about 2 Å, δ is of the order of 10^{-4} to 10^{-5}, depending on the density of the material.

Dynamical diffraction is usually associated with highly perfect single crystals. However, it is interesting to note that some of its concepts were required to analyze this powder problem. It should also be noted that a fundamental premise of kinematic diffraction theory is that all parts of the sample are illuminated by the full unattenuated primary beam; by definition therefore $n = 1$ and the question of refraction cannot arise. In the case of single-crystal diffraction it is well established, both theoretically and experimentally, that Bragg's law

$$2d \sin\theta_L = \lambda \qquad (2)$$

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is exact *only* in the case of symmetric transmission when the Bragg planes are normal to the surface of a plane-parallel crystal plate (James, 1948, 1963). In this paper θ_L is used to indicate the Laue case for symmetric transmission and θ_B the Bragg case for reflection. In principle the peak shift by X-ray refraction varies with f', f'' (or μ) and polarization, and above all the shift in $2\theta_B$ is greatly increased at small incident or diffracted angles to the crystal surface. Measurements of the index of refraction by oblique-reflection Bragg-angle measurements are reviewed by James (1948), while calculations of the dispersion and polarization shifts in Bragg angles have been reported (Hart, 1981).

For perfect crystals the correction to Bragg's law is given in equation (40.10) of the review by James (1963). The diffraction angle $2\theta_B$ becomes

$$2\theta_B = 2\theta_L + \frac{\delta}{\sin 2\theta_L}\left[2 + \frac{\sin(\theta-\chi)}{\sin(\theta+\chi)} + \frac{\sin(\theta+\chi)}{\sin(\theta-\chi)}\right] \tag{3}$$

where χ is the angle between the Bragg planes and the crystal surface. Our experiments are more conveniently concerned with angle α between the incident beam and the sample surface ($\theta - \chi = \alpha$) and we may write instead

$$2\theta_B = 2\theta_L + \frac{\delta}{\sin 2\theta_L}\left[2 + \frac{\sin\alpha}{\sin(2\theta-\alpha)} - \frac{\sin(2\theta-\alpha)}{\sin\alpha}\right]. \tag{4}$$

The refractive index correction δ is typically 10^{-5} at $\lambda = 1$ Å. The magnitude of this correction, $2\theta_B - 2\theta_L = \Delta 2\theta$, is shown in Table 1, which was calculated using $2\theta_L = 40°$ and $\lambda = 1$ Å for various values of α. This table also shows how the measured Bragg angle varies with α. The apparent spacing

$$d' = \lambda / 2\sin\theta_B \tag{5}$$

differs from the true spacing

$$d = \lambda / 2\sin\theta_L. \tag{6}$$

In the absence of anomalous dispersion, δ varies with λ^2 and it turns out that (5) in symmetric *reflection* is an exact equation (James, 1948) but that the constant d' is *not* the spacing between planes. This pseudo-Bragg's law has created many misunderstandings in the past (Thomson & Burr, 1968). The apparent Bragg spacing contraction is, in this example, 86 parts per million and it is therefore only significant in high-precision work.

3. Experimental study

The instrumentation used for the synchrotron-radiation parallel-beam diffractometry has been described previously (Parrish & Hart, 1985). The X-ray optics was greatly improved by use of a longer parallel-slit collimator which gave profile widths of 0·05° (2θ) full width at half maximum (FWHM), as shown in Fig. 1. The peak angles of the narrow symmetrical profiles were determined statistically to 0·0004° using a pseudo-Voigt profile-fitting function and repeated scans were reproducible to 0·001–0·002°. Lattice parameters were derived by least-squares fitting which included only the zero-angle calibration of the diffractometer as a systematic error. There were no other adjustable parameters and no other significant sources of systematic errors were found. The precision of setting the grazing incidence angle α was a few millidegrees.

We have routinely used the NBS standard reference powder materials in our powder diffractometry at the Stanford Synchrotron Radiation Laboratory for wavelength calibration and in the assessment of aberrations and alignment in parallel-beam geometries. The silicon standard which we used in these experiments was a 5–10 μm size sieved fraction from SRM-640 stock prepared with a 1:6 collodion/amyl acetate binder. The samples were 1 mm thick by 22 mm diameter with a carefully smoothed and flattened surface.

As Table 1 shows, a measurement of the refractive index can be made if the apparent Bragg angle $2\theta_B$ is measured for two different angles of incidence α with a fixed wavelength λ. This is the basis of a classical method for X-ray refractive-index measurements (James, 1948, pp. 168–177). We have done the same with SRM-640a silicon powder using a nominal wavelength of 1·75 Å.

Table 2 lists the peak positions of six reflections of the silicon standard obtained with a θ–2θ scan, and with 2θ scans for which $\alpha = 0{\cdot}5$ and 0·25°. The last column shows the deviations between the measured 2θ's and results of a least-squares refinement of data recorded in a θ–2θ run. The refinement also gave the zero-angle correction which was 0·0734, and $\lambda/2a = 0{\cdot}1610991$ (260). The precision of this result is about the same as that claimed for a single measurement of the SRM 640a sample (Hubbard, 1983). Using the

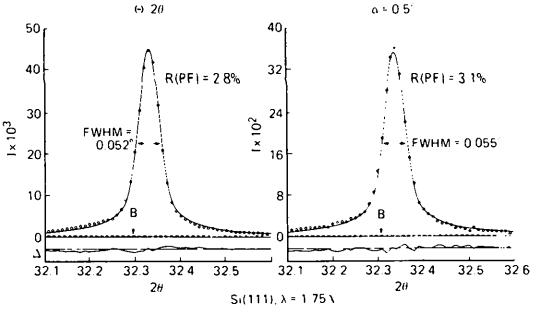

Fig. 1. Typical profile shapes of silicon 111 reflection recorded with θ–2θ scanning (left) and with $\alpha = 0{\cdot}5°$ and detector scanning (right). Differences of profile fitted and experimental points are shown below. $\lambda = 1{\cdot}75$ Å.

Table 1. *Refractive-index correction at* $2\theta_L = 40°$, $\lambda = 1$ Å

α (°)	$\Delta 2\theta$ (°)	α (°)	$\Delta 2\theta$ (°)
20	0·0036	0·5	0·0668
2	0·0176	0·25	0·1324
1	0·0339	0·1	0·3294

Table 2. *Reflection angles* (°) *of silicon computed for profile fitting,* $\lambda = 1·72$ Å

	θ–2θ scan	2θ scan		
hkl	°2θ	$\alpha = 0·5°$	$\alpha = 0·25°$	$\Delta 2\theta$ (°)
111	32·3304	32·3369	32·3372	+0·0029
220	54·1440	54·1506		−0·0021
311	64·5208	64·5284		−0·0003
331	89·1391	89·1340		−0·0039
422	104·1459	104·1547		+0·0036
333	113·5923	113·6024		−0·0002

Table 3. 2θ *shifts* (°) *of silicon caused by refraction* ($\delta = 9·60 \times 10^{-6}$)

hkl	$2\theta_L$	M (0·5°)	C (0·5°)	M (0·25°)	C (0·25°)
111	32·4006	0·0065	0·0651	0·0068	0·1281
220	54·2142	0·0066	0·0644		
311	64·5910	0·0076	0·0642		
331	89·2093	−0·0051	0·0641		
422	104·2161	0·0088	0·0642		
511/333	113·6625	0·0101	0·0642		

recommended NBS value $a = 5·430825\ (36)$ Å for the *powder* value at 298 K with no refractive-index correction we find $\lambda = 1·749732$ Å. Table 2 shows significant but small differences between the measured Bragg angles with different obliquities.

4. Refractive-index calculation

If anomalous dispersion is ignored, the refractive-index decrement for silicon is given by

$$\delta = \frac{-e^2}{2\pi mc^2}\lambda^2\frac{8Z}{a^3}. \qquad (7)$$

For $\lambda = 1·75$ Å, $\delta = -9·6 \times 10^{-6}$. The expected shifts listed in Table 3 were calculated from (4) with the derived values of λ and zero-angle calibration correction. The columns $M(\alpha)$ show the measured shifts in $2\theta_B$ between the θ–2θ setting and the glancing-incidence setting. $C(\alpha)$ is the corresponding value calculated from Bragg's law and corrected for refraction in the usual way. The observed shifts are an order of magnitude less than the calculated values.

The shift is almost independent of *hkl* and Bragg angle. When α is very small, *e.g.* 0·01 rad at glancing incidence, (4) can be written as

$$2\theta_B = 2\theta_L + (2\delta/\sin 2\theta_L) - \delta/\alpha. \qquad (8)$$

Hence $C(\alpha) \simeq \delta/\alpha$, which is independent of *hkl*.

The simplest intuitive explanation of this large difference between experiment and theory is to note that, since the bulk powder is not an optically continuous medium, there will be no refractive-index correction if each power grain Bragg reflects in (nearly) symmetric transmission. Perhaps the refraction effect is determined by the single-particle geometry, *not* by the bulk powder geometry.

Table 4. *Extinction distances and* R_L/R_B *for silicon,* $\lambda = 1·75$ Å

hkl	Δ_0 (μm)	R_L/R_B	*hkl*	Δ_0 (μm)	R_L/R_B
111	16·24	5·05	400	13·83	1·74
220	13·46	2·82	331	18·94	1·52
311	18·27	2·28	422	12·71	1·22

One of the earliest quantitative calculations examined the ray optics (Snell's law) of a spherical particle to obtain a practical refraction-correction algorithm (Wilson, 1940). The main conclusion was that spherical particles add to the X-ray beam divergence. In fact, this can be easily seen: a sphere of radius r is a diverging lens for X-rays because n is less than 1. The focal length f of the lens is given by $r/2(n-1)$ and the maximum beam divergence $2r/f$ equals $4(1-n)\alpha$. For silicon at 1·75 Å wavelength this is 0·0022° and it is independent of the size of the sphere. Another relevant parameter is the angular diameter of the Airy disc formed by Fresnel diffraction. It is $1·22\lambda/r$ which amounts to 0·0022° for a silicon sphere of radius 5·6 μm at $\lambda = 1·75$ Å.

An interpretation of the Ewald/Oseen extinction theorem is that the refractive index is not established until the wave phase shift amounts to, say, $\pi/2$ (Born & Wolf, 1980). The material thickness is then $t < 1/4\Delta_0$ where Δ_0 is the extinction distance. Some extinction distances are given in Table 4 for silicon at $\lambda = 1·75$ Å with linearly polarized radiation. These figures might indicate that the apparent refractive index should not deviate from unity if the particle thickness is less than about 4 μm, $r < 2$ μm.

The question of whether plane-wave or spherical-wave theory is required is also interesting. The radius r of the first Fresnel half-period zone for a wave front at distance R from a point source is given by $r = (R\lambda)^{1/2}$. For laboratory X-rays at 10 cm from the source we find $r = 3·9$ μm if $\lambda = 1·54$ Å and $r = 2·4$ μm if $\lambda = 0·56$ Å. With synchrotron-radiation sources R is more likely to be 25 m, for which $r = 66·1$ μm at $\lambda = 1·75$ Å and $r = 35·4$ μm if $\lambda = 0·5$ Å. If, as in these experiments, $r \simeq 5$ μm we see that synchrotron-radiation experiments and laboratory-based experiments will be under different X-ray optical regimes! The spherical-wave theory is appropriate for the X-ray tube and plane-wave diffraction theory applies to synchrotron radiation.

5. A possible 'theory'

Let us consider the case of a perfect crystal sphere rather than the oxide-coated fracture fragments which

we know all powders to be. An exact equation for the diffracted intensity from an incident wave is complicated by the fact that there will be singularities at the circle of tangential incidence. Two regions are shown in Fig. 2. In region L the diffracted beam is formed in transmission (the Laue case) whereas in the region B (shaped like a lemon slice with an included angle 2θ) the diffracted beam is formed in reflection (the Bragg case). We assume, but will return to the point later, that Zachariasen's (1945) formulae apply, so that in transmission

$$R_L = \pi \sum_{n=0}^{\infty} J_{2n+1}(2A)$$

[equation (3.165) of Zachariasen (1945)]

$$= \pi A \quad \text{for } A \ll 1$$

$$= \pi/2 \quad \text{for } A \gg 1, \tag{9}$$

while in the Bragg case

$$R_B = \pi \tanh A$$

[equation (3.167) of Zachariasen (1945)]

$$= \pi A \quad \text{for } A < 0{\cdot}4. \tag{10}$$

In fact, inspection of the graphs of these functions [Figs. 3.13 and 3.14 in Zachariasen (1945)] shows that his last result is useful up to $A \simeq 1{\cdot}8$ if only 5% accuracy is required. The parameter A is equal to Δ_0/π where Δ_0 is the extinction distance listed in Table 4.

As a first estimate of the refraction correction let us suppose that the correction is the intensity-weighted mean of the symmetric-Laue-case and symmetric-Bragg-case values. Since, within the range of the joint approximations, $R_B = R_L$ in (9) and (10) the intensity ratio for B and L is simply the ratio of the areas illuminated by the Bragg and Laue beams in Fig. 2. Thus

$$\begin{aligned} R_B &\propto 2\pi r^2 F \\ R_L &\propto 2\pi r^2 (1-F) \\ R_L/R_B &= (1-F)/F, \end{aligned} \tag{11}$$

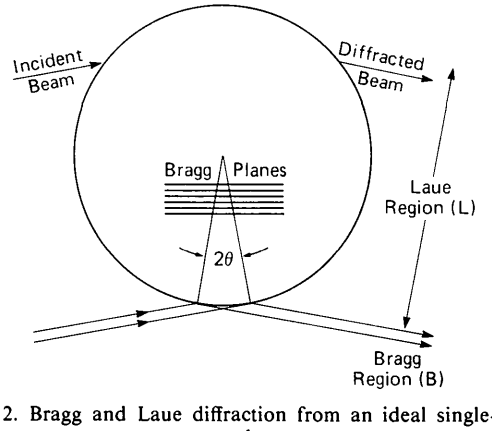

Fig. 2. Bragg and Laue diffraction from an ideal single-crystal sphere.

where F is the fraction of the hemisphere illuminated by the reflected beam B. That area is $(4\pi r^2 2\theta)/2\pi$ so that $F = 2\theta/180$. For $\lambda = 1{\cdot}75$ Å and for the silicon powder we calculate R_L/R_B in colums 3 and 6 of Table 4. The approximations are reasonable for sample thicknesses up to Δ_0/π or about 5 μm according to columns 2 and 5 of Table 4 and indicate that transmitted rays dominate the intensity. Therefore the intensity-weighted refractive-index correction should be much smaller than given by (4).

6. Concluding remarks

It would be unreasonable to draw any quantitative conclusion from the above calculations. They serve, however, to indicate qualitatively that in small-particle powders a reduced refractive-index correction to the Bragg angle is likely. Three regimes can be expected:

(*a*) For the case $r < \Delta_0/\pi$; $r < 2$ μm. The extinction theorem indicates no refractive-index correction to the Bragg angle. This is likely to be the case in all synchrotron-radiation experiments where fine particles are required for statistical reasons.

(*b*) For the case $r \simeq \Delta_0/\pi$; $2 < r < 5$ μm. In this size regime a small refractive-index correction is expected as outlined above. However, since the extinction distance is different for each Bragg reflection, the refractive-index correction will vary in an apparently haphazard way with *hkl* since Δ_0 is a function of the structure factor. For a given λ and *hkl* the correction will depend on particle size.

(*c*) For the case $r \ll \Delta_0$; $r > 25$ μm. The limiting value of R_L in (3) ensures that R_B/R_L becomes greater than one and increases without limit. The effect is accentuated if absorption is taken into account. Large particles will therefore show shifts in Bragg angle caused by refraction and the curvature of spherical surfaces ensures a *larger* correction than indicated by (4). For $r \to \infty$ (4) is exact.

Regrettably, this analysis adds nothing to the basic debate (Hubbard, Swanson & Mauer, 1975; Hubbard, 1983) about why d's derived by powder diffraction are in practice significantly different from those measured by single-crystal methods. We have, however, been able to give clear advice that small enough powder grains should Bragg reflect according to the exact Bragg equation $2d \sin\theta_L = \lambda$ with no refractive-index correction necessary. These small grains will unfortunately be the least perfect representatives of bulk material.

Experiments which show a small or zero effect are perhaps less convincing than those which demonstrate a clear correlation. Our experiments on optically continuous films of various iron oxides do show large Bragg-angle shifts at glancing incidence which are entirely compatible with the predictions of (4). We have confidence therefore in the importance of

these null results with silicon powder. It is clear from other measurements (*e.g.* electron microscopy) that powder grains are not prefect crystals, even if they happen to be spheres.

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The Two-Dimensional Quasicrystallographic Space Groups with Rotational Symmetries less than 23-Fold

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Abstract

The crystallographic concepts of lattice and space group are extended to describe materials with crystallographically forbidden point groups, and a complete classification of all two-dimensional space groups with rotational order less than 23 is given.

1. Introduction

The complete classification of the symmetries of periodic crystals, carried out in the nineteenth century by Bravais, Fedorov, Schoenflies and others, is an essential tool for determining and describing the structures of materials with diffraction patterns consisting of Bragg peaks. The classification is organized by the 32 crystallographic point groups (ten in two dimensions), which specify the symmetry of the macroscopic translationally invariant features of crystals - crystal habit, responses to external perturbations *etc.* Within this classification the description of the 14 Bravais lattices and 230 space groups in three dimensions (five and 17 in two dimensions) relies heavily on periodicity, as specified by the real-space lattices which describe the microscopic translational symmetries of crystalline materials.

Quasicrystalline materials have point groups which are incompatible with periodicity; their diffraction patterns consist of sharp well defined Bragg-like peaks, arranged with crystallographically forbidden point-group symmetries. The absence of periodicity precludes their description in terms of the standard classification system. We present here a reformulation of the concepts of space groups and lattices which, while reducing to the conventional scheme in the crystallographic case, is general enough to provide a classification of quasicrystalline materials by their lattices and space groups. This generalization is entirely based in reciprocal (wave-vector) space, where quasicrystals and crystals have the common

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