

Accuracy in Temperature Factor Determination in Powder Diffractometry

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Abstract

The discrepancy between the temperature factors derived from X-ray powder diffraction and those derived from X-ray single crystal or neutron powder diffraction led us to look for additional causes of systematic intensity errors for powders. Integrated intensities of powder diffraction lines were carefully measured for selected materials using a Bragg-Brentano powder diffractometer equipped with an automatic divergence slit and a graphite monochromator. The measured intensities were compared with calculated intensities and significant systematic effects were observed which could not be related to structural sources, but were traced to instrumental sources. Use of an empirical angular dependence correction factor resulted in acceptably low R values. The instrumental factor couples strongly to the temperature factor by virtue of a similar angular dependence. Thus, reliable temperature factors cannot be obtained from commercial powder diffractometers unless the instrumental contributions are first removed.

1. Introduction

Wilson (1970) noted that an overall temperature factor term is useful in the refinement process in addition to a general scaling factor which is the same for all the observed reflections. Recent years have witnessed great improvements in data collection and sample preparation methods. New automatic X-ray powder diffractometers measure integrated intensities with an accuracy of $\pm 0.5\%$ (Parrish and Huang 1983). Many materials are now available in spheroidal and very fine particle powder form to fulfil the requirement of X-ray intensity measurements (Hubbard 1983*a*, 1983*b*).

The combination of digital data collection with line profile fitting procedures yielded fairly low R values for powder materials (Will *et al.* 1983). However, whereas the atomic positions from X-ray powder diffractometry are very close to those obtained from X-ray single crystal data, there are significant differences in the atomic thermal vibrating parameters. Moreover, it seems that in neutron diffractometry there is no such gap.

Corundum (α -Al₂O₃) has been used as a standard reference material for intensity measurements in powder diffraction (Hubbard 1983*a*, 1983*b*; Dragoo 1986). Its structural parameters are known accurately from single crystal diffractometry (Calvert *et al.* 1981; Lewis *et al.* 1982). The two positional parameters which have been found by powder methods are in good agreement with the single crystal data. Neutron diffraction shows similar anisotropic (Jorgensen and Rotella 1982) and isotropic temperature factor data (Cooper *et al.* 1980; Cox *et al.* 1980; Will *et al.*

1982). The data on X-ray powder temperature factors found by Debye-Scherrer geometry with Cu K β radiation (Thompson and Wood 1983) and by the conventional Bragg-Brentano diffractometry (Will *et al.* 1983; Hill and Madsen 1984) are in poor agreement with the single crystal data. Several causes for the systematic errors have been mentioned in several papers, such as the peak shape of the K α doublet (Thompson and Wood 1983), and poor counting statistics (Hill and Madsen 1984). These authors noted that the parameters used in the profile fitting procedures, the selection of the shape function and the weighting, may affect the angular behaviour and cause incorrect temperature factors (Will *et al.* 1983; Hill and Madsen 1984). Thus it seems that the discrepancy between single crystal and powder temperature factors can be attributed to additional factors causing systematic errors.

In the present work we collected integrated intensity data from flat samples in a Bragg-Brentano diffractometer. We used an automatic divergence slit in order to improve the counting statistics at high Bragg angles. We used three different materials and changed the counting statistics by reducing the thickness of the samples. We also changed the surface quality in some solid samples. The materials which were selected—corundum, molybdenum and tungsten—have known atomic positions; thus, the overall temperature factor is left as a single unknown parameter to be derived by structure refinement from the relative intensity data. We believe that our results add to the knowledge on the accuracy of temperature factor determination by conventional X-ray powder diffractometry.

2. Experimental

Our data were collected by a commercial Philips PW-3720 automatic powder diffractometer consisting of a long fine-focus Cu X-ray tube powdered by an XRG-3100 generator, routinely operated at 40 kV and 40 mA, a theta-compensated slit which includes an integral Soller collimator of $\pm 2.3^\circ$ axial divergence, a 0.2 mm receiving slit followed by a curved graphite monochromator, a secondary Soller collimator (also $\pm 2.3^\circ$ divergence) between the receiving slit, and the monochromator. The sample is illuminated over a length of 13 mm (fixed) and a width of 15 mm. The counting electronics chain consists of the standard Philips PW-1710 system which compensates for pulse height shifts up to about 500 000 counts per second. The maximum count rate observed for corundum was about 12 000 counts per second. With a dead time of less than 1 μ s, corrections were less than 1%. Careful alignment was carried out prior to measurement to minimise effects from misalignment (Schreiner 1986).

The experiments for the present study were carried out with α -alumina (corundum) consisting of very fine and round crystallites, prepared by the American National Bureau of Standards (NBS) as a standard reference material and called 'SRM-674', with fine powders of molybdenum and tungsten, and with electromechanically polished surfaces of solid tungsten (sintered) with a grain size of 5–10 μ m. The particles sizes were less than 1 μ m in corundum and 2.5 μ m in the other powders.

Some of the samples were prepared as thin transparent specimens in order to test the effects of transparency aberrations and counting statistics. To insure random orientation and uniform density we prepared most of the specimens from an equal mixture of powder to vaseline by volume. We compared the intensities of these samples with packed powders (bulk samples) and the same relative intensity distribution has been found. The thin samples were prepared by smearing the powder-vaseline over

a holder. In the case of the corundum the holder was a solid polycrystalline silicon disk-shaped piece. The sample transparency was measured by the attenuation of the Si substrate diffraction intensities. We used the equation

$$i = I \exp(-2\mu t \sin \theta), \quad (1)$$

where i is the intensity of the Bragg angle θ from the Si substrate for a sample with thickness t and linear absorption μ , and I is the diffraction intensity from the free silicon surface ($\mu t = 0$) under the same conditions. The transparency here is characterised by the product of μ and t , designated by $(\mu t)_{\text{Si}}$.

Integrated $\alpha 1$ plus $\alpha 2$ intensities were obtained from a slow scan over selected peaks with linear background subtraction. The scan generally ranged from 2.5° to 4.0° , depending on the nearness of interfering peaks. The background was measured at the extreme ends of each scan range. The count time for the background was 20 s at each point measured to eliminate counting statistics errors. More details about the measuring method are given elsewhere (Schreiner and Kimmel 1987).

Integrated intensities were compared on a relative scale to values calculated from structure data using a program written by Kimmel (1985). The program computes the contributions from Lorentz polarisation, the diffracted beam monochromator, the variable divergence slit, and the structure factors including anomalous dispersion and temperature factors. The version for the present work used the absorption and the overall temperature factor as values which can be derived by refinement. The observed intensities were scaled such that $\Sigma I_{\text{obs}} = \Sigma I_{\text{cal}}$ and all intensities had the same weight. The intensity R value was calculated from

$$R = \frac{\Sigma |I_{\text{obs}} - I_{\text{cal}}|}{\Sigma I_{\text{obs}}}. \quad (2)$$

The overall temp. factor modifies the calculated intensity by $\exp(-2B \sin^2 \theta / \lambda^2)$ and the absorption correction modifies it by the term $\{1 - \exp(-2\mu t / \sin \theta)\}$, where μ is the average linear absorption factor and t the sample thickness. The transparency term found by refinement is designated by $(\mu t)_r$. During the refinement process we were able to look for the best fit of the calculated data by modifying B and $(\mu t)_r$ either separately or simultaneously.

3. Results and Discussion

The refinement of the samples is made by using an additional overall temperature factor correction in the range $-1.0 < \delta B < +1.5 \text{ \AA}^2$ and the absorption correction term $\{1 - \exp(-2\mu t / \sin \theta)\}$, where μt ranges from 0 to 6 (6 is practically infinite). We found that with the same goniometer three kinds of systematic errors exist; namely, positive, negative or null.

(a) Corundum

The results for the corundum samples are summarised in Fig. 1. All bulk samples showed negative systematic errors (i.e. the observed intensities at the higher 2θ angles were lower than expected). Starting with temperature factors of zero for the aluminium and oxygen atoms, an overall temperature factor of $0.95(5) \text{ \AA}^2$ was found for a bulk packed powder sample (without medium), and the R value was

2.1%. The above overall temperature factor value is equivalent to the addition of $\delta B = 0.72(5) \text{ \AA}^2$ to the single crystal isotropic atomic thermal vibration data from Lewis *et al.* (1982, LSF). When the monochromator was removed, the overall temperature factor decreased to 0.75 \AA^2 , equivalent to $\delta B = 0.52 \text{ \AA}^2$ above the LSF data, but R increased to 2.5%.

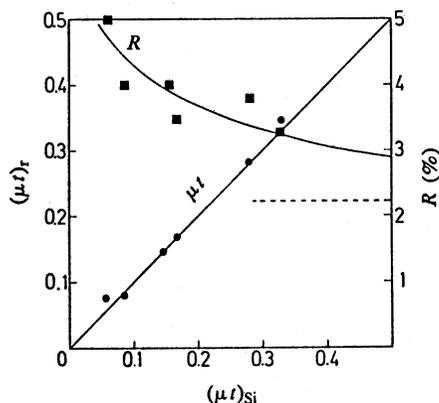


Fig. 1. Plot of R and $(\mu t)_r$ versus $(\mu t)_{Si}$ in thin corundum samples. The samples were taken from an equal ratio mixture of corundum powder and vaseline. Further, $\delta B = 0.63 \text{ \AA}^2$ and the correction term for the monochromator is $(1 + 0.9 \cos^2 2\theta)$ rather than $(1 + 0.8 \cos^2 2\theta)$.

Table 1. Structural parameters for corundum

Space group $R\bar{3}c$ (167) (hexagonal axes). Cell dimensions: $a = 4.7598 \text{ \AA}$ and $c = 12.9917 \text{ \AA}$. Atomic coordinates: Al, $z = 0.3520$ and O, $x = 0.3062$. Temperature factors: $B(\text{Al}) = 0.23 \text{ \AA}^2$ and $B(\text{O}) = 0.20 \text{ \AA}^2$. Monochromator term: $(1 + 0.9 \cos^2 2\theta)$.

Sample description	$I(021)$ (c.p.s.)	$(\mu t)_{Si}$	$(\mu t)_r^A$	δB^B (\AA^2)	R (%)
Bulk packed powder	727	—	∞	0.63	2.1
Bulk without monochromator	782	—	∞	0.52	2.5
Thick mixture (vaseline)	631	—	1.7	0.63	2.1
Thin mixture (1 mm)	541	1.5	1.4	0.66	3.4
Thin mixture (0.25 mm)	439	0.32	0.35	0.56	3.2
Thin mixture	430	0.28	0.30	0.53	3.5
Thin mixture	384	0.176	0.178	0.55	3.3
Thin mixture	377	0.152	0.156	0.54	3.9
Thin mixture	236	0.083	0.088	0.54	3.7
Thin mixture	219	0.058	0.076	0.44	4.7

^A For $\delta B = 0.63 \text{ \AA}^2$. ^B For $(\mu t)_{Si}$.

Since a lower δB factor is needed for the correction of the systematic intensity errors in the absence of a monochromator, it is worth while to reprocess the data using the last modifications for the angular dependence of intensity with a graphite monochromator (Jennings 1984). The term $(1 + 0.8 \cos^2 2\theta)$ was replaced by $(1 + 0.9 \cos^2 2\theta)$, and we found that for bulk packed powder $\delta B = 0.632 \text{ \AA}^2$ with $R = 2.1\%$. The correlation between $(\mu t)_{Si}$ and $(\mu t)_r$ was maintained. It should be noted that alternatively, we could calculate δB for each μt value assuming that $(\mu t)_{Si}$ which has been measured directly is fixed, and then calculate the δB by refinement at each sample. We found δB to be in the range $0.54\text{--}0.58 \text{ \AA}^2$ for most samples, which is a close fit to the case without a monochromator. The results are shown in Table 1.

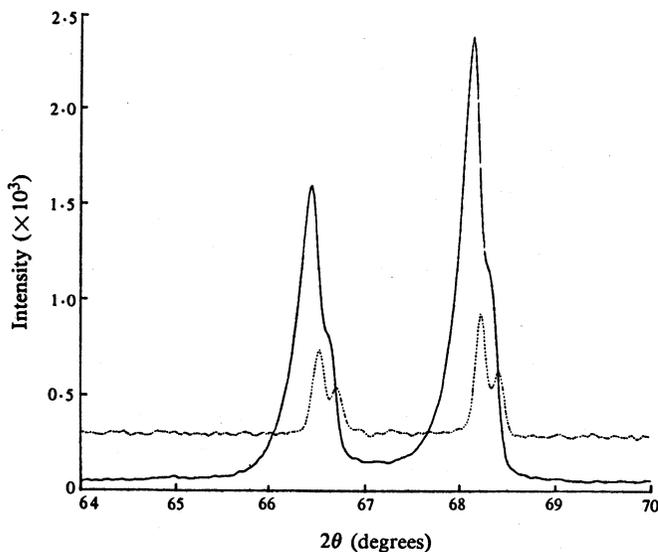


Fig. 2. Comparison between diffractograms of thin (dotted curve) and bulk (solid curve) samples. The samples were taken from an equal ratio mixture of corundum powder and vaseline.

In the thin corundum samples the counting statistics were poor in comparison with the bulk samples. This could increase both the random and the systematic errors (Hill and Madsen 1984). We found that the goodness of fit decreased gradually when the samples became more transparent (Table 1 and Fig. 1), but the systematic error was independent of the sample thickness. It seems that the use of the automatic divergence slit helped to keep equally distributed strong reflections along 2θ angles (Jenkins and Paolini 1974; Kimmel 1987). It should be noted that thin samples have less transparency aberrations, resulting in sharper peaks (see Fig. 2), but this did not reduce the systematic errors.

With a general overall temperature factor term $\delta B = 0.63 \text{ \AA}^2$ for all corundum samples added to the single crystal (LSF) data, we see that $(\mu t)_r$ and $(\mu t)_{Si}$ are completely matched (Table 1). Fig. 1 shows a linear dependence of $(\mu t)_r$ and $(\mu t)_{Si}$ for $\delta B = 0.63 \text{ \AA}^2$, demonstrating the correlation between these factors. However, R becomes lower when the sample becomes thicker.

(b) Molybdenum

Table 2 shows the results of X-ray diffraction from a bulk sample of molybdenum powder, mixed with vaseline (with equal volume ratios). A very low error ($R = 0.25\%$) was achieved (Table 2a). The overall temperature factor of 0.188 \AA^2 is within the range of the reported data (Lonsdale 1962). Using the modified term for the monochromator with the molybdenum samples we found the same calculated value of $(\mu t)_r$, but the overall B factor was 0.14 \AA^2 instead of 0.19 \AA^2 (Table 2b). The results of using the conventional and the modified terms for the monochromator are given in Table 3.

Thin samples of similar mixtures resulted in the same temperature factor, but the total R value was increased dramatically in the transparent samples (Fig. 3).

we suggest that positive intensity systematic error (systematic increase with 2θ angle) is caused by granularity effects. Similar to Suortti (1972), we probably got that the high μd values (where μ is the linear absorption coefficient and d is the particle size) are accompanied by an increase in the reflectivity at high θ values due to surface roughness.

A theory of microabsorption of X-ray intensity in packed powders was recently presented (Hermann and Ermrich 1987), modifying earlier treatments (Wilchinsky 1951; Harrison and Paskin 1964; Suortti 1972). According to this theory, the correction factor for the relative intensities in the corundum powder is θ -independent because the particle size is less than $1 \mu\text{m}$ compared with the penetration depth value of $45 \mu\text{m}$. Thus, the negative systematic error found in the corundum is assumed to be due to instrumental effects. These aberrations are of the same trend as evaluated by Suortti and Jennings (1971), but the observed deviations are much larger than those calculated. This disagreement calls for additional study.

Table 5. Overall temperature factors for the NBS SRM-674 set

Material	Crystal size (μm)	Penetration depth (μm)	B (\AA^2)	R (%)
Al_2O_3	<1	44.9	0.84	3.3
TiO_2	1-2	21.2	1.20	1.0
ZnO	1-2	20.2	0.94	2.1
Cr_2O_3	1-2	6.2	1.00	1.8
CeO_2	1-2	1.7	0.60	0.7

Table 6. Summary of microabsorption phenomena in the present study (for powders only assuming a packing factor of $\alpha = 0.5$)

Shown are the overall, Debye-Waller, instrumental and microabsorption values. Values in the first three columns are rounded

Sample	$B(\text{ov})$	$B(\text{DW})$	$\delta B(\text{instr})$	$\delta B(\text{ma})$	α	μd	Calculated roughness (μm)
Bulk corundum	0.9	0.2	0.7	0	0.5	0.1	—
Thin corundum	0.8	0.2	0.7	-0.1	0.5	0.1	0.7
Molybdenum	0.2	0.2	0.7	-0.5	0.5	0.4	1.0
Tungsten	-0.1	0.1	0.7	-0.7	0.5	0.8	0.7

Using the method of Hermann and Ermrich (1987), the contribution of the microabsorption phenomena to the angular intensity distribution was calculated. We assumed a packing factor of 0.5, and used μd values taken from the mean particle size of each sample. Then we calculated the amount of roughness which causes a shift of the overall B relative to the value which includes only the thermal vibration and instrumental aberrations. This shift is estimated to be -0.5\AA^2 in the molybdenum powder and -0.7\AA^2 in the tungsten powder. Apparently, thin samples of corundum also showed a shift of -0.1\AA^2 (see Table 1) which may be attributed to the increase of the contribution of the surface to the intensity relative to the bulk. The results of the treatment using the Hermann and Ermrich formulation are given in Table 6. The roughness is found to be near $1 \mu\text{m}$ for all types of powders, which is close to the particle size in corundum and half the particle size in molybdenum and tungsten.

The solid samples showed that the surface quality is more important than individual grain size. Polycrystalline samples with grain size of 50 μm had a systematic error more negative than 2 μm powders. The flat surface of the individual grains in solid samples exhibits a different geometry in which the primary absorption correction is less severe in comparison with the round powder. Since the solid samples are not perfectly randomly oriented, the R values were greater than those of the powders. The solid samples are unsuitable for the study of intensity systematic errors because their relative intensity is sensitive to the surface quality.

5. Conclusions

(1) In our para-focusing diffractometer, flat sample intensities have a negative systematic error, equivalent to an additional temperature factor of $\delta B = 0.60(5) \text{ \AA}^2$. This error probably arises from the term used to calculate the angular dependence of the intensity and is rather deviated from the real case. For example, without the monochromator, the systematic error decreased, indicating that the monochromator correction term $(1 + \cos^2 2\theta \cos^2 2\alpha)$ is an approximation to a more complicated general formula (Azaroff 1955). The goodness of the approximation also depends on the individual monochromator crystal (Jennings 1984). The selection of a precise term for the monochromator may change the calculated B factor by up to 0.1 \AA^2 when 2θ angles are between 20° and 90° .

(2) The thin corundum samples showed that neither penetration depth nor the counting statistics are major reasons for intensity aberrations.

(3) If the powder is not very fine or if the surface is not very smooth, primary absorption affects the diffraction spectrum, causing a positive systematic error which compensates the basic instrumental effect.

(4) The advantage of the single crystal technique is that the geometry of the diffracted crystal is known, and while applying a proper absorption correction, the main reason for the systematic error is the temperature factor. In powders, we have a variety of crystal shape and size, and the exact correction for the primary absorption effect of the individual grain is unknown. Thus, the temperature factors are only one of several reasons for systematic errors. It was shown here that without treating the other factors which affect the angular intensity behaviour, the B values derived from the relative intensity of a single powder diffraction run are not the true Debye-Waller factors.

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