

Precision of determination of d -spacings using a Guinier camera

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Abstract. The precision of determination of lattice spacings using a commercial triple Guinier camera and a precision comparator is evaluated. Determination of lattice constants on germanium, tungsten and various samples of mullite are given. It is found that d -spacings can be routinely determined with uncertainties of the order of 1 part in 10000 in the analytically most useful Bragg angle range from 0 to 45° in theta.

Keywords. Precision; d -spacings; Guinier camera.

1. Introduction

For a perfect camera the uncertainty in d -spacing measurements is given by the expression: $\Delta d/d = \cot \theta \Delta \theta$, assuming that the wavelength of the x-ray beam is either known accurately or is considered a reference value. For cubic crystals the relative uncertainty of the lattice constant $\Delta a/a$ likewise varies as $\cot \theta \Delta \theta$. It has become standard practice to determine lattice constants for cubic and other crystals using extrapolation methods as the uncertainty of a d -spacing measurement should vanish at $\theta = 90^\circ$. Details on determination of lattice constants using powder measurements, and references are given by Klug and Alexander (1974).

The standard Guinier camera employing transmission geometry normally limits the angular range to $\theta_{\max} = 45^\circ$. Extrapolation methods are of little use in this case. Precision determinations require very accurate angle measurements. Since a good Guinier camera gives very sharp lines when a suitable sample is employed, it should be possible to obtain accurate d -spacing when using Guinier techniques. Most powder lines which are suitable for identification purposes are located in the "Guinier range", and it is of practical importance, especially for analytical purposes, to examine the accuracy obtainable with the Guinier camera, especially as it is of much lower cost than a powder diffractometer and as it has a better resolving power than a standard diffractometer.

Using a Guinier camera the Bragg angle θ is determined by measuring the distance l between the line from the primary beam and the powder line from a given d -spacing. For a camera of diameter 114.592 mm the nominal θ -value is found as $\theta(\text{degrees}) = l(\text{mm})/4$ and $\Delta \theta(\text{degrees})$ should accordingly be given as $\Delta l(\text{mm})/4$. Film shrinkage and other sources of error, such as lack of reproducibility of sample to film distance, require calibration of the film, *e.g.* by using a reference sample with accurately known lattice constants for accurate determinations of d -spacings.

We have been using a comparator yielding nominal uncertainty of 0.2 μm in measuring l -values. This uncertainty is far below other uncertainties connected with d -spacing measurements, and we assume therefore that the reproducibility of our d -spacing measurements reflect the sum of other errors connected with the methods applied such as imperfection in camera construction and deviations from linearity in film shrinkage and the like.

2. Experimental

We use an Enraf-Nonius FR 552 Guinier camera with a Philips fine-focus (0.4×8 mm) x-ray tube. The camera has three compartments allowing simultaneous exposure of three samples. Pure $\text{CuK}\alpha_1$ radiation is used in all three compartments.

The comparator was made by Zeiss, Jena, and was modified according to Tomkins and Fred (1951) and Bennet and Koehler (1959). Line positions can be read with a nominal uncertainty of $0.2 \mu\text{m}$ and peak intensities can be determined over a range from 1 to 100. Our samples have been exposed at $22\text{--}24^\circ\text{C}$. No strict temperature control has been kept. Thermal expansion coefficients of many simple inorganic compounds are of the order of magnitude of $10^{-5}/^\circ\text{C}$. An indeterminacy of $1\text{--}2^\circ$ would allow $\Delta d/d$ to be approximately 10^{-4} for most "hard" substances.

In the past, we have used one compartment in our triple Guinier camera for the reference sample and corrected θ -values in the two other compartments using the calibration values obtained from our standard. However, when the comparator became available to us, we found that this procedure is not valid when the precision of measuring l is better than 0.1 mm. Therefore we now mix our reference material with the sample when high accuracy is required. Normally, we use semiconductor grade silicon, and when silicon is not well suited we use germanium. Unfortunately, germanium powder is quickly contaminated by GeO_2 and only freshly powdered germanium is a suitable reference material. Although we can normally reproduce readings to the nominal uncertainty of $0.2 \mu\text{m}$ when repeating measurements of a given line within a short time scale of a few minutes, the reproducibility of measuring lines on a given film at different days is about $0.005\text{--}0.01$ mm. Corrections from different exposures can vary as much as 0.1 mm.

For comparison we have also used a standard Bragg-Brentano type powder diffractometer equipped with a diffracted beam graphite monochromator and a strip chart recorder. We use Co-radiation with the diffractometer and both the α_1 and the α_2 components are registered. The diffractometer allows angles to be measured up to 158° .

3. Discussion

The corrections $\Delta\theta$ can be reproduced within an uncertainty of about 0.01 mm by a polynomial of second degree. We have tried two expressions:

$$\Delta\theta = a + b\theta + c\theta^2 \quad \text{and} \quad \Delta\theta = \frac{a \cdot \theta + b}{1 + c\theta}$$

and determined a , b and c by ordinary least-squares methods using a microcomputer.

In principle, $\Delta\theta$ should vanish at $\theta = 0$. Experience shows, however, that it is advantageous to include a constant term in the expressions. In most cases there is little difference between the applicability of the two expressions. Some care must, however, be exercised when using the hyperbolic expression as " c " is normally negative and a singularity sometimes occurs.

The validity of our approach has been checked by measurements on high purity samples of germanium and of tungsten using semi-conductor grade silicon as reference sample. Lattice constants were calculated both by using $(tg\theta)^2$ as weights and by using unit weights. No significant difference was found, although the weights differ with a

factor of 10 when the $(tg\theta)^2$ weighting scheme is used.

For comparison the lattice constants were determined also from powder diffractometer measurements using an instrument allowing measurements up to 158° in 2-theta. Peak positions were read from strip chart recordings. Also in this case we used silicon as an internal standard.

The lattice constants were also in this case calculated using both $(tg\theta)^2$ weighted and unweighted data. The range of weights in this case was from 1–120 (W) and 1–28 (Ge). The $(tg\theta)^2$ weighting scheme has some similarity with an extrapolation procedure. The lattice constants for Ge and W determined by both methods are given in table 1. There are no significant differences between the lattice constants obtained by the two methods.

As a further check, we tried to distinguish between two samples of mullite of slightly different compositions. Mullite is a crystalline phase composed of Al_2O_3 and SiO_2 . It exists in the interval 60–67 mole % Al_2O_3 . The literature gives conflicting information on the melting of mullite. Some authors claim that the melting is congruent, others that it melts incongruently. References on such observations and a phase diagram of Al_2O_3 , SiO_2 are given by Aramaki and Roy (1959).

Neuhaus and Richartz (1958) have grown single crystals of mullite of composition $2Al_2O_3$, SiO_2 by the Czochralski method. This supports the assumption of congruent melting. We have also at Aarhus succeeded in growing transparent mullite crystals of 2:1 composition by Czochralski growth using an iridium crucible to contain the melt.

The quality of these crystals was assessed by neutron and x-ray diffraction. We were not, however, able to grow single crystals from melts of composition $3Al_2O_3$, $2SiO_2$. These experiments gave invariably a polycrystalline mass. We examined the differences in lattice constants between 2:1 and 3:2 mullites by powder diffraction using both the Guinier camera and the powder diffractometer. In both types of measurements silicon was added as internal standard.

Precision measurements of Guinier diagrams of the two samples showed small but significant differences. All *d*-spacings of the 2:1 sample were larger than the corresponding ones from the 3:2 sample. The differences varied from 0.0176 Å for the largest *d*-spacing measured (5.41 Å) to 0.0011 Å for the smallest spacing (1.24 Å). Expressed in theta-angles the difference varied from 0.04 to 0.1 degrees.

The powder diagrams were indexed preliminarily using lattice constants obtained

Table 1. Lattice constants of Ge and W by Guinier and diffractometer methods using Si as reference material. $CuK\alpha_1 = 1.540598$ Å, $CoK\alpha_1 = 1.78890$ Å. Lattice constant, *a*, of Si = 5.43083 Å.

Method	No. of lines	Radiation	Weighting scheme	Sample	<i>a</i> (Å)	σ_a Å
Guinier	5	$CuK\alpha_1$	$(tg\theta)^2$	Ge	5.65844	6.39×10^{-4}
Guinier	5	$CuK\alpha_1$	unit weights	Ge	5.65859	1.03×10^{-3}
Diffract.	7	$CuK\alpha_1$	$(tg\theta)^2$	Ge	5.65700	7.31×10^{-4}
Diffract.	7	$CuK\alpha_1$	unit weights	Ge	5.65661	1.31×10^{-3}
Guinier	3	$CuK\alpha_1$	$(tg\theta)^2$	W	3.1651	3.57×10^{-3}
Guinier	3	$CuK\alpha_1$	unit weights	W	3.1652	4.62×10^{-3}
Diffract.	6	$CoK\alpha_1$	$(tg\theta)^2$	W	3.16459	1.58×10^{-4}
Diffract.	6	$CoK\alpha_1$	unit weights	W	3.16454	2.23×10^{-4}

Table 2. Lattice constants of two mullite samples. One of composition $2\text{Al}_2\text{O}_3, 1\text{SiO}_2$ (2 : 1 mullite) and another of composition $3\text{Al}_2\text{O}_3, 2\text{SiO}_2$ (3 : 2 mullite). Silicon was used as reference sample. Values of constants employed are given in table 1.

Method	No. of lines	Radiation	Weighting scheme	Sample	a (Å) $\sigma_a (\times 10^{-3})$	b (Å) $\sigma_b (\times 10^{-3})$	c (Å) $\sigma_c (\times 10^{-4})$
Guinier	35	$\text{CuK}\alpha_1$	$(tg\theta)^2$	2 : 1 mullite	7.5927 1.86	7.6840 1.78	2.8882 3.56
Guinier	35	$\text{CuK}\alpha_1$	unit weights	2 : 1 mullite	7.5924 1.88	7.6841 1.86	2.8882 3.86
Guinier	37	$\text{CuK}\alpha_1$	$(tg\theta)^2$	3 : 2 mullite	7.5748 1.75	7.6836 1.94	2.8857 3.43
Guinier	37	$\text{CuK}\alpha_1$	unit weights	3 : 2 mullite	7.5750 1.76	7.6838 1.92	2.8857 3.62
Diffraet.	19	$\text{CoK}\alpha_1$	unit weights	2 : 1 mullite	7.5852 1.8	7.6831 2.5	2.8878 7
Diffraet.	16	$\text{CoK}\alpha_1$	unit weights	3 : 2 mullite	7.5745 2.15	7.6839 1.5	2.8855 7

from measurements on a Picker four-circle diffractometer on a single crystal. Thirty seven reflections could be indexed unambiguously and these were used in a least-squares analysis for determinations of lattice constants. Standard deviations of the Guinier data are smaller than those from the diffractometer data. The data are given in table 2.

4. Conclusion

It is possible to determine d -spacings of high accuracy, $\Delta d/d \approx 10^{-4}$ in the analytically most important angular range using a commercially available Guinier camera, provided that the powder lines are measured with a precision corresponding to an uncertainty of θ of about 0.002 – 0.005° . Although our comparator is hand-operated, the measuring process is not unduly time-consuming. Automated equipment does exist and Edmonds and Henslee (1978) report on the use of microcomputer-controlled film densitometry applied to Guinier films. Their results are comparable with ours. Computing facilities need not be very sophisticated for handling computations like evaluating measurements, indexing lines and making least-squares determinations of lattice constants. We employ a microcomputer with 48 K bytes memory and two floppy disk drives, but also a smaller computer could do most of the computations. Search/match procedures are often helped by the high precision of the data and the cost of a Guinier camera + comparator + microcomputer is lower than that of a powder diffractometer of similar capacity.

Acknowledgements

I am indebted to the Carlsberg Foundation for providing the cost of the microcomputer and to Mrs B Lundtoft for assistance in data collection.

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