Acta Cryst. (1978) A**34**, 484–489

A Simple Bragg-Spacing Comparator

By M. Ando,* D. Bailey† and M. Hart‡

H. H. Wills Physics Laboratory, Royal Fort, Bristol BS8 1TL, England

(*Received* 20 *October* 1977; *accepted* 30 *November* 1977)

A simple Bragg-spacing comparator is described which achieves a routine precision of 3 parts in 10^8 in lattice-spacing measurements. One conventional X-ray source and three detectors are required and measurements take only 10 min. The instrument is used to survey the lattice-parameter variations in silicon crystals manufactured by many different suppliers since 1965.

Introduction

Conventional methods of determining the lattice parameter of crystals rely on assumed values for the wavelengths of characteristic X-ray lines and in principle measure the Bragg angle θ for a particular wavelength. The Bragg spacing d is then determined from Bragg's law

$$2d \sin \theta = \lambda.$$

Corrections may be required for X-ray refraction and absorption and, depending on the method, allowances may be necessary for systematic errors of an essentially geometric nature. Ultimately, the precision of measurement is limited to a few parts in a million by the intrinsic X-ray line width, though with adequate care, the lattice parameters of crystals of the same material can be compared to within a few parts in ten million (Baker, George, Bellamy & Causer, 1966).

The fundamental spectral linewidth limitation is removed in pseudo-non-dispersive methods (Hart, 1969) which all rely on the fact that double-crystal rocking curves (obtained with almost equal crystals) are very narrow and are not appreciably influenced by the width of the source spectrum. In practice the limit of precision is set solely by counting statistics and by instrumental drift, but the apparatus required may be both expensive and complicated. There is obvious scope for designing pseudo-non-dispersive diffractometric methods in which simplicity, low cost and speed are gained at the expense of precision. The first development in this direction was made by Larson (1974) for sensitive and rapid measurements of changes in the lattice parameter of copper as a function of neutron dose. Larson's method was later applied to gallium arsenide (Baker, Hart, Halliwell & Heckingbottom, 1976), using a germanium reference crystal to measure variations in stoichiometry and in impurity concentration.

The new method which we describe here has the advantages that both the reference crystal and the sample crystal have simple shapes, that the instrumental requirements are simple and inexpensive and that measurements can be made quickly. It has the disadvantage that the range of lattice parameter covered is smaller than in any of the earlier methods, but this has not proved a limitation in practice in the experiments on silicon which we shall describe. We shall also indicate how this restriction can be overcome.

Principle of the method

The comparator works over a small range of lattice parameter usually with the reference crystal and sample made from the same material but differing in purity, strain, stoichiometry, vacancy concentration *etc.* Ideally the reference crystal would be a perfect crystal but that is not essential. Indeed, in these experiments the reference crystal was impure. The method relies on measuring the difference in sample angle between the doubly reflected peak D and the triply diffracted peak T (Fig. 1*a*). Provided that only small differences are involved we may assume that the optical constants of the reference crystal and sample are the same. Then differences in Bragg angle are entirely due to changes in atomic spacing. Suppose, for a moment, that the single-crystal reflectivity function (the Darwin–Prinz curve) is symmetrical and that both crystals are homogeneous. This is the case of zero absorption. Then, by symmetry arguments we see that the T beam has its maximum when the Bragg planes are parallel, thus establishing the origin $\omega = 0$ of the sample angle scale. The D-beam peak occurs when $\omega = \theta_S - \theta_R$. The difference in lattice parameter $\Delta d = d_S - d_R$ is

$$\Delta d/d = -\cot \theta \, \Delta\theta = -\cot \theta \, (\theta_S - \theta_R). \quad (1)$$

---

* Present address: Department of Applied Physics, University of Tokyo, Bunkyo-Ku, Tokyo 113, Japan.

† Present address: New South Wales Institute of Technology, Broadway, New South Wales, Australia 2007.

‡ Present address: Department of Physics, King's College, Strand, London WC2R 2LS, England.

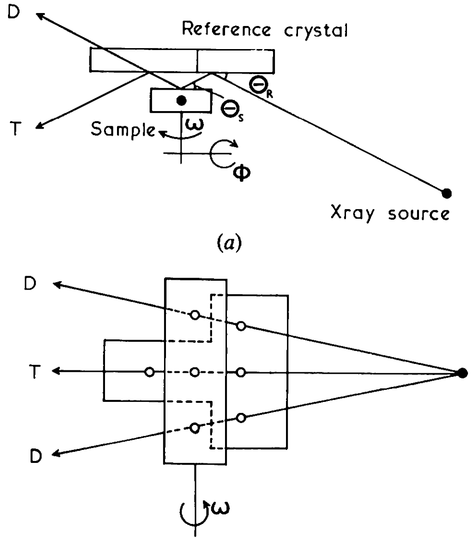
In practice, the crystal absorption ensures that the *T* beam is not symmetrical, but the effect is small and can be calculated if necessary since all of the X-ray optical constants are known. The reference crystal requires only a flat surface large enough to accommodate the reference beams. In common with other back-reflection methods, only a small exposed surface is required on the sample – the end of a whole boule, for example, could be measured without the destructive preparation of slices.

In some situations the equivalent Laue-case arrangement has advantages. Since both *D* and *T* beams are usable in the equatorial plane in the Laue case two detectors may suffice.

Experimental arrangement

The planar arrangement indicated in Fig. 1(*a*) cannot be realized in practice because the absorption of the reference crystal is too high. A simple modification overcomes this problem. As Fig. 1(*b*) shows, the triply reflected beam lies in the horizontal plane (normal to the goniometer axis) and two double-diffracted beams are used, inclined at equal angles above and below the horizontal plane. The mean angular position of these two beams determines the position of a virtual *D* beam in the horizontal plane.

The goniometer axis consists of a spindle supported in an elastically preloaded pair of ball bearings which is driven by a stepping motor through a folded lever system. One motor step is approximately 0·0385 s of arc. Tilts about an axis ϕ, in the Bragg planes and normal to the goniometer axis, are controlled to about 2 s of arc by a 100 mm tilting arm which is spring loaded against a micrometer screw. The tilting arm is also mounted on a spindle supported by a pair of elastically preloaded ball bearings. The collimator consists of three pinholes each 0·5 mm in diameter, spaced 6 mm apart and 340 mm from the 0·4 mm diameter effective X-ray source. Thus, the *D* beams were inclined at $\gamma = \pm 0{\cdot}0176$ rad to the horizontal plane. The length of the collimator is determined by the need to resolve one spectral line and γ must be large enough to provide adequate tilt sensitivity. As will be clear later, the dimensions chosen are not critically important. Since the (local) lattice-spacing reference is maintained in those parts of the reference crystal which are illuminated by the X-ray beams it is important that the pinholes are fixed with respect to the reference crystal and that the gap between reference and sample remains constant throughout a series of measurements.



(*a*)

(*b*)

Fig. 1. (*a*) Plan and (*b*) elevation showing the experimental arrangement.

In these experiments the 444 Bragg reflection of Mo $K\alpha_1$ radiation was used throughout but we shall see later that the sensitivity can be adjusted to suit the problem to hand by choosing other combinations of Bragg reflection and X-ray wavelength. The outputs from the three detectors are automatically recorded on paper tape while the diffractometer is driven in a step-scan mode. Temperature fluctuations are adequately controlled by enclosing the whole apparatus in a box made from polystyrene foam since long-term temperature drifts have no effect on these pseudo-null experiments. In practice, transient thermal effects are easily detected because the three intensity curves, recorded *simultaneously* show correlated steps. Such fluctuations were never observed once the thermal enclosure had been installed. Each experiment lasted less than 10 min to achieve a precision of a few parts in 10^8 for $\Delta d/d$.

Because the sample requirements are simple, and because the experimental time is so short, we were able to undertake a survey of many silicon crystals. The results are important for the establishment of X-ray length standards. The method has applications for the non-destructive quantitative analysis of the concentration of impurities, point defects, irradiation damage, strains caused by applied fields and the determination of non-stoichiometric variations in crystals.

Experimental results

The reference crystal was cut from a dislocation-free, vacuum-float-zoned silicon crystal (Texas Instruments Lopex silicon; sample No. 7). The orientation of the reference surface was (111) ± 20 s of arc and was cut normal to the growth axis so that the surface layer was homogeneous. Table 1 shows the lattice parameters which were deduced, in the zero-absorption approximation, from the angular separation of the *D* and *T* beams. In each case the beam position was calculated as the centroid of the intensity histogram, truncated at about ±3 peak widths (at approximately 1% of peak intensity for the *D* beams). A truncation correction was made according to the method of Thomson & Yap (1968).

Crystal No. 17 in Table 1 is a hyperpure, carbon and oxygen-free crystal, PERFX, grown by Dow Corning Corporation almost ten years ago. We had insufficient material to use PERFX as a reference crystal, but the relative lattice parameters are shown in the last column of Table 1.

All of the other floating zone (*F*) crystals contain carbon as an impurity and their lattice parameters are smaller than that of the purer PERFX. It is interesting to recall that Baker, Tucker, Moyer & Buschert (1968) found that six of their PERFX crystals had a fractional range of lattice parameter of only $8 \pm 3 \times 10^{-8}$ with a mean deviation of only 2×10^{-8} over the six samples. We may assume that our sample of PERFX has the same lattice parameter as theirs to better than one part in ten million.

In at least six countries around the world one can obtain, on a commercial basis, carbon-contaminated float-zoned silicon which is dislocation free and whose lattice spacing is independent of supplier to better than seven parts in ten million. The samples measured in this survey differed from PERFX by between −0·34 p.p.m. and −1·03 p.p.m.

Table 1. *Lattice-parameter variations in the silicon crystals from different suppliers*

F grown by the floating-zone method, *C* Czochralski method. Probable error $\pm 3 \times 10^{-8}$.

No.	Sample	Identification	Growth method	$d - d_{\text{ref}}$ ($\times 10^8$)	$d - d_{\text{PERFX}}$ ($\times 10^8$)
1	Lopex	10632	*F*	14	−34
2		10669	*F*	−28	−76
3		10669	*F*	−7	−55
4		11434	*F*	−10	−58
5		32327	*F*	8	−40
6		32327	*F*	−35	−83
7		32949	*F*	5	−43
8		32949	*F*	2	−46
9		38643	*F*	−12	−60
10		38704	*F*	−30	−78
11		38704	*F*	2	−46
12		39539	*F*	−33	−81
13	Wacker	51704/6	*F*	−7	−55
14	Hoboken	7390/2	*F*	−25	−73
15		7390/2	*F*	14	−34
16	Philips		*F*	−325	−373
17	PERFX		*F*	48	0
18	Haldor Topsøe		*F*	−16	−64
19	Toshiba		*F*	−1	−49
20			*C*	273	225
21	Mullard		*F*	−55	−103
22			*C*	359	311
23	Russian		*C*	427	379
24	IBM		*C*	347	299

Czochralski-grown silicon contains oxygen as the dominant impurity and so has a larger lattice spacing than purer silicon (Table 1). In our (small) sample we straddle the world market and the survey shows that growth conditions are sufficiently similar that Czochralski-grown dislocation-free silicon will have a lattice parameter which is likely to be +3 p.p.m. ± 1 p.p.m. greater than that of hyper-pure silicon.

Sample 16 is a special case. The sample has been heat treated in a hydrogen atmosphere (de Kock, 1971) so as to render it homogeneous ('swirl-free') after doping and as a consequence its lattice parameter is nearly 4 p.p.m. smaller than that of hyper-pure silicon.

Systematic errors

We have experimentally delineated the range of alignment errors which influence the measured Bragg-angle variations.

(*a*) *Errors arising from beam and crystal tilts*

Larson (1974) has given a detailed geometric theory of the errors arising when the plane of rays is not symmetrical with respect to the first crystal and when the tilt angle ϕ between the two crystals is not zero. In practice we were able to adjust ϕ sufficiently well that misalignments are not the determinants of errors in $\Delta d/d$. Fig. 2(*a*) shows rocking curves obtained with sample No. 8 when properly aligned. At 40 kV and 4 mA the peak counting rate was about 500 s^{-1} and the full widths at half height are 0·54 s of arc and 0·13 s of arc for the *D* and *T* peaks respectively. The angle scale marks are at intervals of 10 motor steps. When the tilt ϕ is 10 s of arc from the parallel position the two *D* peaks occur at different angles as Fig. 2(*b*)

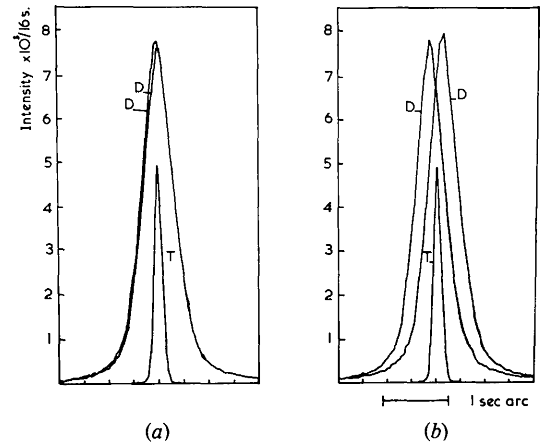


Fig. 2. Rocking curves obtained with (*a*) well aligned and (*b*) slightly misaligned crystals. 444 Bragg reflection of Mo $K\alpha_1$ radiation at 40 kV, 4 mA. Sample No. 8.

shows. But there is no detectable change in the full widths at half height of the three peaks.

Even when the upper and lower D beams were separated by one peak width, they were both symmetrical within the errors of counting statistics. Since the two D-beam collimator pinholes were equidistant from the central pinhole to within normal machining tolerance (± 10 μm), we assume that the two D-beam rocking curves are equally displaced from the angular position of the virtual D-beam rocking curve (which would be obtained with the beam which passes through the central pinhole). In practice, after final alignment, the separation of the two D-beam rocking curves was always less than 10% of their widths and this introduces an error in the measurement of $\Delta d/d$ which is less than 2 parts in 10^8, as Fig. 3 shows. In those cases $\phi \lesssim 2$ s of arc. It is clear from Fig. 2 that errors in tilt of more than 2 s of arc are clearly visible in the three rocking curves.

An estimate of the influence of misalignments was made experimentally on sample No. 8. The variation with tilt of 'apparent lattice parameter', derived from (1), is linear as Fig. 3 shows. From the 14 measurements made with good alignment we find that the mean $\Delta d/d$ is $+2 \times 10^{-8}$ and that the standard deviation for a single measurement is $\pm 3 \times 10^{-8}$. The measured slope of the graph is in agreement with estimates based on Larson's (1974) geometrical theory.

(*b*) *Refractive-index corrections*

The Bragg angle of a crystal depends upon the angle between the crystal surface and the Bragg planes. The potential error due to X-ray refraction has been explored in detail before (Hart, 1969). In these experiments the refraction error is quite negligible since all the crystal surfaces were cut and polished to within 20 s of arc of the (111) planes.

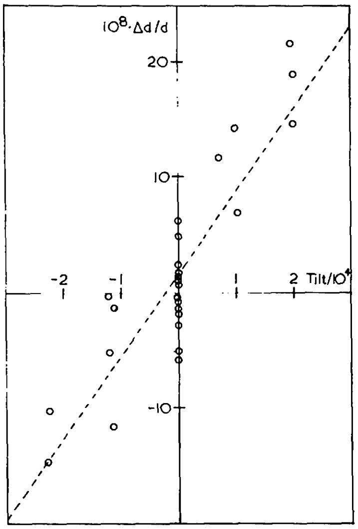


Fig. 3. Measurements of the apparent Bragg spacing when the tilt setting is not correct.

(*c*) *Truncation errors*

A considerable portion of the integrated intensity resides in the tails of the Bragg peaks. Since, for simplicity, we have calculated centroids there exists in principle a truncation error when the data points are not symmetrically disposed about the peak.

We have systematically investigated the influence of truncation errors by calculating centroids with various degrees of truncation. As one would expect, the centroid position obtained in the general case when the truncation is asymmetric with respect to the peak (the peak itself is symmetric) varies as the truncation limits are changed. In practice, the truncation was always within one data-point (0·0385 s of arc) of symmetric truncation and the D peaks were approximately 14 data points (0·5 s of arc) wide at half maximum intensity. Under these conditions we found that the centroid position is insensitive to the truncation position. Over the range of truncation from ± 1 s of arc to $\pm 2{\cdot}5$ s of arc the mean D-peak centroid shifted by only 0·002 s of arc, corresponding to an error of 2×10^{-8} in $\Delta d/d$. The T beam, which has very little intensity in the flanks, shifts by only 0·003 s of arc over the same range of truncation.

We conclude that the simplest method of peak location is appropriate in this case since the errors introduced are no larger than the inherent errors of misalignment (*a*) and the error implicit in the zero-absorption approximation. More complicated methods of peak location would be justified only when combined with a detailed theoretical analysis of the T-beam shape.

(*d*) *Temperature control*

Because these are comparative rather than absolute measurements, the usual requirements for temperature control are considerably relaxed. Measurements of lattice parameter to 2 parts in 10^8 imply temperature stability to 8 mK for silicon (and to 1–5 mK for most other materials). But even with a low-power X-ray source the total measurement time was less than 10 min per data set. The two crystals are physically quite close together so that the sensitivity to temperature gradients is small. A polystyrene-foam enclosure provides entirely adequate thermal control under normal laboratory conditions, provided of course that the X-ray source, motors and detectors are not inside it.

Range of sensitivity and the choice of X-ray optical conditions

In practice, once the pinholes, detectors and their apertures have been correctly positioned, the T beam could be measured even when it was several peak-widths (say ± 2 s of arc) away from the D beam. Thus, the present arrangement, which uses the 444 Bragg reflection of Mo$K\alpha_1$ radiation, can be used over a range of $\Delta d/d = \pm 2 \times 10^{-5}$. The resolution in $\Delta d/d$ is 2×10^{-8} and this is 0·05% of the range. By choosing different Bragg reflections and different X-ray wavelengths, both the range and sensitivity can be altered though their ratio remains constant at about 2000 to 1. At longer wavelengths the influence of X-ray absorption on peak shape will become greater than it is at short X-ray wavelengths.

The range is fundamentally determined by the range of Bragg reflection $\Delta\Psi_0$ and by the usual relation between lattice-parameter difference $\Delta d/d$ and Bragg-angle change (1). Now

$$\Delta\Psi_0 \propto \lambda^2 F_{\mathbf{h}}/\sin 2\theta \propto -\frac{\Delta d}{d} \tan\theta \tag{2}$$

so that both the range and sensitivity of comparison are determined by

$$\Delta d/d \propto d^2 F_{\mathbf{h}} \tag{3}$$

where $F_{\mathbf{h}}$ is the structure factor.

Whereas the 444 Bragg reflection gives a measurement range of about 40 p.p.m., the 111 reflection could be used to measure $\Delta d/d$ up to almost 0·1% and the 777 reflection would provide a measurement range of about 5 p.p.m., with a sensitivity of a few parts per billion. Using Mo $K\alpha_1$, Cr $K\alpha_1$ and Ag $K\alpha_1$, respectively (the Bragg angle is roughly the same for each of the three Bragg reflections), one piece of apparatus and a single {111} reference crystal would conveniently cover the range of lattice parameters $10^{-9} < \Delta d/d < 10^{-3}$.

Homogeneity and symmetry of silicon

In two series of experiments we were able to investigate the gradients of lattice parameter along the growth axis of a single crystal and the Bragg spacings of symmetry-related planes.

Samples 2 and 3 (Table 1) were 17 cm apart in the as-grown crystal. Samples 7 and 8 were only 2 cm apart. Unfortunately we do not know which member of a pair was closest to the seed and we do not know the total length of each crystal. Crystal lengths of 50 cm are quite common and on this basis it appears that the variations within a single crystal are perhaps 2 or 3 times smaller than the differences between crystals obtained from the same manufacturers at different times and are also rather smaller than the differences between crystals grown by different manufacturers. It would be fascinating to explore the origin of these variations in terms of impurities, vacancies and isotopic abundance; but that would require detailed technical information which is not available to us.

In the case of Texas Instruments material (Lopex) we can conclude that over a period of about ten years the output of one manufacturer varied within a total range of only 0·5 p.p.m. Comparing their material with similar material grown by other manufacturers *world wide* the total range is still only 0·6 p.p.m. It is well established that carbon is the main cause of this variation and that in carbon-free material (Baker *et al.*, 1968) the differences between crystals grown by the same manufacturer may vary by only 0·08 p.p.m. The time is almost ripe for a new survey of the so called 'swirl free' material which has become available in the last year or two though, if sample 16 is typical, we may well find that the lattice parameter of this material is less reproducible than that of hyper-pure material such as PERFX and perhaps even less reproducible than the standard float-zoned material has been.

Table 2 shows the lattice-parameter variations in a set of four crystals with {111} surfaces, which were cut from the reference crystal, No. 7 in Table 1. The growth axis was [111] and the tetrahedron from which the four samples were cut was smaller than 2 cm on each side.

Table 2. *Lattice-parameter variations in a set of four crystals with* {111} *surfaces, which were cut from the reference crystal*

Orientation	$d - d_{\text{ref}}$ ($\times 10^8$)
$[111]$	2
$[11\bar{1}]$	−33
$[1\bar{1}1]$	12
$[\bar{1}11]$	13

Since the sum of the lattice-parameter deviations is zero within the experimental error (approximately 3 parts in 10^8 in each measurement) these results may indicate that the silicon structure is distorted but that the volume of the unit cell is unchanged. The result can be stated in a different way; we may find that two samples of ordinary float-zoned silicon could have the same unit-cell volume, and thus the same density, and yet could differ in lattice parameter (on one plane only) by up to 0·5 p.p.m. This result has important implications for experiments designed to measure Avogadro's Number.

A distributable X-ray standard?

Following Baker *et al.* (1968) we may conclude that the high-purity PERFX crystals were extremely consistently prepared. The standard deviation of six crystals was approximately ±0·012 p.p.m. One crystal of PERFX was measured by X-ray and optical interferometry (Deslattes & Henins, 1973) to give $d_{2\bar{2}0}$ (25 °C) = 1·9201715 Å ± 0·30 p.p.m. and this was later confirmed as 1·9201718 Å ± 0·25 p.p.m. (Deslattes *et al.*, 1974) but altered to 1·9201706 Å ± 0·15 p.p.m. (Deslattes, Henins, Schoonover & Carroll, 1976) following the correction of a systematic error. Under vacuum the Bragg spacing is 0·34 p.p.m. larger. Since this precision is far below the reproducibility of PERFX and is comparable with the range of lattice parameters measured in Table 1 for float-zoned silicon, it would seem that any source of such silicon could be used to access the absolute value of lattice spacing. IR absorption measurements can be used to measure the carbon concentration and the necessary correction is (Baker *et al.*, 1968) $\Delta d/d = -6{\cdot}5 \times 10^{-24} n_{\rm C}$ where $n_{\rm C}$ is the number of carbon atoms per cm^3.

At a rather lower precision one can have access to the PERFX lattice parameter by using Czochralski-grown oxygen-contaminated silicon. After IR determination of the oxygen concentration the lattice-parameter shift can be calculated from $\Delta d/d = +3{\cdot}8 \times 10^{-24} n_{\rm O}$ where $n_{\rm O}$ is the number of oxygen atoms per cm^3.

Within the errors of measurement all of the values in the right-hand column of Table 1 are therefore effectively on the absolute scale.

Hubbard, Swanson & Mauer (1975) have recently announced that a large quantity of powdered float-zoned silicon has been made available for calibration purposes in powder diffractometry. Since they were only concerned with *reproducibility* to 10 p.p.m. and not with absolute lattice spacings, it seems that the important attribute of this proposed standard is not the manifestly well defined lattice parameter of the starting material but the ill defined quality of the resultant powder. The wording of their recommendation that one uses 'the powder diffraction value of 5·430880 Å for the *lattice parameter* of the Standard Reference Material silicon' is amazing. The lattice parameter of Deslattes *et al.* (1976) for PERFX was 5·43106446 Å ± 0·15 p.p.m. in vacuum.

One of the authors is pleased to thank the British Council for a scholarship. The automatic diffractometer system was constructed with a grant from the Paul Instrument Fund. We are especially grateful to John Burrow who oriented, cut and polished all of the samples and to those listed in Table 1 who provided samples of silicon for this survey.

References

BAKER, J. A., TUCKER, T. N., MOYER, N. E. & BUSCHERT, R. C. (1968). *J. Appl. Phys.* **39**, 4365–4368.

BAKER, J. F. C., HART, M., HALLIWELL, M. A. G. & HECKINGBOTTOM, R. (1976). *Solid-State Electron.* **19**, 331–334.

BAKER, T. W., GEORGE, J. D., BELLAMY, B. A. & CAUSER, R. (1966). *Nature* (*London*), **210**, 720–721.

DESLATTES, R. D. & HENINS, A. (1973). *Phys. Rev. Lett.* **31**, 972–975.

DESLATTES, R. D., HENNINS, A., BOWMAN, H. A., SCHOONOVER, R. M., CARROLL, C. L., BARNES, I. L., MACHLAN, L. A., MOORE, L. J. & SHIELDS, W. R. (1974). *Phys. Rev. Lett.* **33**, 463–466.

DESLATTES, R. D., HENINS, A., SCHOONOVER, R. M., CARROLL, C. L. & BOWMAN, H. A. (1976). *Phys. Rev. Lett.* **36**, 898–900.

HART, M. (1969). *Proc. R. Soc. London Ser. A*, **309**, 281–296.

HUBBARD, R. C., SWANSON, H. E., & MAUER, F. A. (1975). *J. Appl. Cryst.* **8**, 45–48.

KOCK, A. J. R. DE (1971). *J. Electrochem. Soc.* **118**, 1851–1856.

LARSON, B. C. (1974). *J. Appl. Phys.* **45**, 514–518.

THOMSON, I. S. & YAP, F. Y. (1968). *Acta Cryst.* A**24**, 702–705.

Acta Cryst. (1978). A**34**, 489–491

Absorption-Weighted Mean Path Lengths for Spheres

BY H. D. FLACK AND M. G. VINCENT

Laboratoire de Cristallographie aux Rayons X, Université de Genève, 24 *quai Ernest Ansermet, CH-*1211 *Genève* 4, *Switzerland*

(*Received* 7 *November* 1977; *accepted* 3 *December* 1977)

Accurate values (~0·05%) of the absorption-weighted mean path lengths for spheres as a function of μR and θ have been calculated by differentiation of the table of values of absorption corrections [Dwiggins (1975). *Acta Cryst.* A**31**, 395–396].