ation shown in Fig. 5. An unpolarized beam of nominal wavelength λ is incident upon a polarizing multilayer set at the appropriate Bragg angle. The spin-up neutrons are reflected while the spin-down neutrons are transmitted (the multilayer can be deposited on either a single substrate or a Soller array of substrates of highly transparent single-crystal Si or sapphire). The transmitted beam is subsequently back-scattered at exactly 90° from a mosaic crystal placed within a flat-coil spin flipper. The flipper field is adjusted so that within the coil a neutron makes an adiabatic $\pi/2$ turn before and a $\pi/2$ turn after being reflected. (The coil thickness can be made large compared to the average penetration depth of a neutron into the crystal.) The back-scattered neutron now in the 'up' eigenstate is subsequently deflected by the multilayer towards the sample (or, as shown in Fig. 5, a vertically focusing PG crystal and then to the sample). The spin-up neutrons in the incident beam, on the other hand, will be first reflected by the multilayer and upon back-scattering from another crystal undergo a π spin turn and be transmitted through the multilayer in the same direction as the original incident spin-down neutrons. The advantage of this arrangement is that the exact back-scattering geometry is maintained without the problems normally encountered in using an ordinary deflection crystal in the incident beam, which would deflect incident neutrons equally as well as back-scattered neutrons. Also, if needed, a polarized beam can be obtained by simply shutting off one or the other π-flipper.

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A New Approach to the Measurement of X-ray Structure Amplitudes Determined by the *Pendellösung* Method

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Abstract

The Laue-case rocking curve from two thin crystals is known to exhibit fine structure which can be used to determine the corresponding structure amplitude F_h. Thus F_{444} and F_{777} have been measured for crystalline silicon to a standard deviation of 0·2%. F_{444} is in excellent agreement with published experimental values. There are no previous high-precision measurements of F_{777} in the literature. The values measured

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seem to indicate that the accepted theoretical dispersion corrections are somewhat too low. A highly stable monolithic thin-wafer silicon diffractometer of a novel design was employed. Using an energy-dispersive solid-state detector and the white spectrum of a tungsten X-ray tube, rocking curves from a number of planes of the *hhh* family could be recorded simultaneously, thus reducing measurement time considerably and minimizing the influence of some sources of systematic and random error. Least-squares computer fitting of the theoretical curve to the complete measured one is employed to determine the value of F_h from the data. A complete discussion of the method is presented.

1. Introduction

The electron distribution in single-crystal silicon has recently received much experimental (Hatori, Kurlyama, Kategawa & Kato, 1965; Tanemura & Kato, 1972; Aldred & Hart, 1973*a*, *b*; Kikuta, 1971; Hart & Milne, 1970; Bonse & Teworte, 1980; Cusatis, Hart & Siddons, 1983) and theoretical (Dawson, 1967*a*, *b*; Price, Maslen & Mair, 1978; Pietsch, 1980) attention. The availability of large single crystals of silicon with a very high degree of perfection enabled high-precision experimental structure-factor measurements based on the dynamical theory of crystal diffraction to be carried out. The most complete set of structure factors F_h for silicon published to date was measured by Aldred & Hart (1973*a*, *b*) for most Bragg reflections up to 555. Their values were calculated from the spacings of photographically recorded *Pendellösung* fringes generated by characteristic X-rays in a wedge. The mean standard deviations obtained for the highest-order planes measured were 3 to 8 me (millielectrons). Accuracies of ~5 me were also obtained by Tanemura & Kato (1972) who used a combination of interferometric and *Pendellösung* methods, again, with photographic detection, to deduce values of F_h for a few low-order Bragg planes. Some of their values, however, deviate from those of Aldred & Hart (1973*a*, *b*) by as much as 20 me.

Very recently, Bonse & Teworte (1980) deduced values of F_h for the 440 reflection for two characteristic wavelengths by fitting the extrema of the outer wings of the oscillatory rocking curve measured in a separated-crystal Laue–Laue diffractometer to the same quantities on the asymptotic expansion of the theoretical curve. The mean standard deviations obtained were larger than 23 me and the asymmetry of the published rocking curves indicated serious drifts even for this low-order, and relatively wide, 440 reflection.

We present here experimental values of F_h for the 444 and 777 reflections at several different wavelengths, with accuracies of 3–9 me, obtained from rocking curves measured using a novel type of monolithic thin-wafer Laue–Laue diffractometer. The better than $0{\cdot}001''\,d^{-1}$ stability (Cusatis, Hart & Siddons, 1983) of the diffractometer was sufficiently high to render undetectably small smearing and asymmetry in the measured curves due to drifts. Thus, a multi-parameter non-linear least-squares fit of the theoretical curve to the *complete* measured rocking curve becomes feasible. All relevant parameters, including the wafer thicknesses and the structure factor are obtained from the analysis, to an accuracy considerably higher than that achievable in a separate measurement of the crystal thicknesses. An energy-dispersive mode of operation, using the continuous radiation from a W tube and a Ge detector, allows simultaneous measurements of a number of harmonic rocking curves in the same *hkl* family, thus reducing appreciably the measurement time and eliminating some common sources of error.

The method is presented in the next section and the experimental details in the third one. The results obtained for F_h are given in the last section.

2. The method

2.1. *Theory*

In the symmetric Laue geometry used in this experiment, and for a weakly absorbing crystal, *i.e.* $\mathrm{Re}(\chi_h) \gg \mathrm{Im}(\chi_h)$, where χ_h is the complex electric susceptibility, the intrinsic reflection curve for a plane having a reciprocal-lattice vector **h** is given by (Pinsker, 1978)

$$I_R(y) = [\exp(-\mu t/\cos\theta_B)/2(1+y^2)] \times \{\cosh[\mu t\varepsilon(1+y^2)^{-1/2}/\cos\theta_B] - \cos[2\pi t/\Delta_0)(1+y^2)^{1/2}]\}, \quad (1)$$

where μ, t and θ_B are the linear coefficient of absorption, the crystal thickness and the Bragg angle, respectively. y and Δ_0 are the deviation from the centre of the reflection curve in multiples of half the Darwin width for the given plane and the extinction length, respectively. They are given by

$$y = (\theta - \theta_B)\sin 2\theta_B / C|\chi_{hr}| \quad (2)$$

$$\Delta_0 = \lambda \cos\theta_B / C|\chi_{hr}|, \quad (3)$$

where θ is the glancing angle, λ is the wavelength and C is the polarization factor.

$$C = \begin{cases} 1 & \sigma \text{ polarization} \\ |\cos 2\theta_B| & \pi \text{ polarization.} \end{cases}$$

For silicon, which has a diamond lattice, the complex susceptibility χ_h can be written as

$$\chi_h = \chi_{hr} + i\chi_{hi} = (r_e\lambda^2/\pi\Omega)|F_h| + i(\mu\lambda/2\pi)\varepsilon, \quad (4)$$

where r_e is the classical electron radius, Ω the unit-cell

volume, F_h is the temperature-modified structure factor and $\varepsilon = \varepsilon_0 \exp[-B(\sin\theta_B/\lambda^2]$ is the temperature-modified ratio $|\chi_{hi}|/|\chi_{0i}|$. The Debye parameter $B = 0{\cdot}4680$ for silicon at room temperature (Price, Maslen & Mair, 1978). ε_0 is given by (Hildebrandt, Stephenson & Wagenfeld, 1975)

$$\varepsilon_0 = \begin{cases} a_g[1-2Q\sin^2\theta_B)] & \sigma \text{ polarization} \\ a_g[(1-Q)\cos 2\theta_B & \\ \quad +Q\cos 4\theta_B] & \pi \text{ polarization,} \end{cases}$$

where $a_g = 1$ if all indices of the plane used are even, $a_g = 2^{-1/2}$ if all indices are odd and $a_g = 0$ for any other combination. For a given crystal and wavelength Q is a constant related to the photoelectric absorption coefficient and, to a very good approximation, linearly dependent on the energy of the X-rays used.

The first term in the curly brackets in (1) is a smoothly decreasing function of y. The second term, however, oscillates with a period dependent on t/Δ_0. For $t \gg \Delta_0$ it oscillates very rapidly with t and thus small unavoidable t variations across the beam cross section smear out the pattern. I_R, therefore, becomes the smooth bell-shaped curve observed in the Borrman effect. In the other limit, $t \ll \Delta_0$, the first minimum of the oscillating term occurs for $y \gg 1$ where I_R is already very small due to the $(1+y^2)^{-1}$ term in front of the curly brackets. In practice, therefore, a smooth curve is also obtained in this limit. If, however, t is such that $\mu t < 1$ and t/Δ_0 is of order unity the oscillations occur for values of y where the intensity is appreciable and are therefore observable experimentally (Lefeld-Sosnowska & Malgrange, 1969). Note, however, that even low-order reflection curves are only of order 1″ wide, so that fine structure is extremely difficult to observe using a single Laue reflection since the exploring beam must have an effective angular divergence considerably smaller than the rocking-curve width. We have, therefore, chosen to use a double-crystal configuration. For a two-crystal Laue–Laue diffractometer the measured intensity is the convolution of two intrinsic reflection curves:

$$I(\Delta) = I_0 \sum_{\sigma,\pi} \int I_R^{\sigma,\pi}(\theta) I_R^{\sigma,\pi}(\theta+\Delta)\,\mathrm{d}\theta, \qquad (5)$$

where Δ is the angular offset between the two crystals, I_0 is the intensity of the beam impinging on the first crystal and the summation is carried over both polarization states. Owing to the oscillatory nature of I_R, $I(\Delta)$ also exhibits fine structure with features having, under favourable conditions, angular widths one to two orders of magnitude smaller than the total width of the rocking curve. As the details of the shape of $I(\Delta)$ depend strongly on the value of F_h, a fit of the theoretical $I(\Delta)$ curve to the measured rocking curve can, in principle, yield the value of F_h without recourse to thickness measurements. This is the basic idea behind the method presented here.

2.2. *Diffractometer design*

The very sharp features of the rocking curves and their intrinsically small Darwin widths for high-order reflections put very severe demands on the diffractometer. Extreme long-term stability and very high immunity to vibrations and temperature variations are mandatory. Means must be provided to obtain a smooth precise and high angular resolution (<0·001″) in the rotation of one crystal relative to the other. Finally, the two crystals of the diffractometer have to be aligned perpendicular to the plane of diffraction to a high precision and maintain their relative alignment for long periods.

A simple and elegant solution that satisfies the above requirements is found in a monolithic diffractometer. It is carved entirely out of a single perfect silicon crystal, as shown in Fig. 1. The two diffracting wafers of the diffractometer are machined out of the silicon block. A leaf spring is cut between the wafers and a rotation of one wafer relative to the other is achieved by bending this spring using the force between a small electromagnet and a small permanent magnet attached to the silicon blocks which carry the wafers. The small size and single-material construction of the instrument minimize temperature gradients and facilitate thermal isolation and temperature control. The non-contacting electrical, rather than mechanical, rotation method does not generate any vibrations of its own and inhibits the transfer of outside vibrations to the crystal. The 'two crystals' of the diffractometer are inherently aligned and the elastic hinge serves as an accurate backlash-free and smooth axis of rotation: the resulting parasitic translation of one wafer with respect to the other is of no consequence in these measurements.

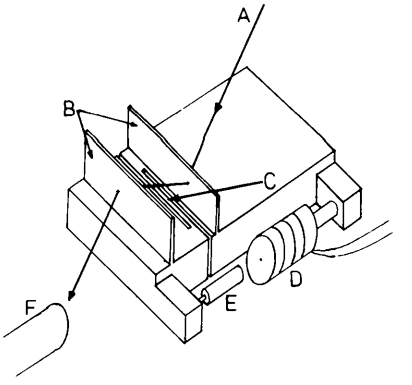

Fig. 1. The monolithic diffractometer. *A* X-ray beam, *B* wafers, *C* leaf spring, *D* electromagnet, *E* permanent magnet, *F* solid-state detector.

2.3. *Data collection and analysis*

As mentioned above, the details of the fine structure in the rocking curve depend very sensitively on the value of the structure factor F_h, but also on the thicknesses t_1 and t_2 of the two wafers of the diffractometer. If these thicknesses are known, it is possible, in principle, to calculate the value of F_h from the measured rocking curve. In practice, however, determination of F_h to ~0·1% requires measurements of t_1 and t_2 to ~0·05%. For a wafer $t \simeq \Delta_0$ thick this means thickness measurements to sub-micrometre accuracies for X-ray wavelengths ~1 Å. Furthermore, non-contact methods are preferred since the crystal surface must not be subjected to mechanical damage. The extreme difficulty in achieving such accuracies is reflected in the F_h results of Bonse & Teworte (1980) where the 0·25% accuracy in thickness measurements limited the accuracy of their F_h values to a mean standard deviation of 0·5%, even for the insensitive low-order 440 Bragg reflection.

It should also be noted that, while the elastic hinge discussed above provides a smooth rotation which is linear (Siddons, 1979) in the current supplied to the coil, the absolute magnitude of this rotation is not known. Independent calibration of the angle/current characteristic has so far not been feasible at the necessary precision. The conversion factor depends on the physical dimensions of the leaf spring, the elastic modulus of the crystal and the geometry and construction of the permanent magnet–electromagnet pair. Determination of F_h to an accuracy of 0·1% requires the knowledge of the rotation caused by a given current in the coil to about the same accuracy.

Two procedures for data collection and analysis were developed to cope efficiently with the difficulties discussed above. The first, more conventional, procedure consists of measuring a series of rocking curves for a family of Bragg planes using characteristic radiation. At least one of the planes is chosen to be a previously measured one so that its F_h is known to a high precision (Aldred & Hart, 1973*a*, *b*). The theoretical curve of (5) is then fitted to the data collected for this plane holding F_h fixed at its known value and t_1, t_2 and the conversion factor from current steps to seconds of arc left as the parameters to be optimized. Once this conversion factor is obtained, (5) is fitted in turn to each of the data sets collected for the other planes holding the current step–angle conversion factor fixed and optimizing t_1, t_2 and F_h. Note that the wafer thicknesses t_1 and t_2 are different in this procedure for each plane since, for different Bragg angles, the beam hits the wafers at different points and the wafers are never homogeneous in practice to the necessary precision.

The second procedure is an energy-dispersive one whereby the Bragg angle is first fixed using a characteristic line and a plane for which F_h is known, then the X-ray tube is replaced by a W tube without disturbing the angular setting. Using the continuous radiation from the tube and a high-energy resolution Ge detector each of the harmonics transmitted by the crystal is fed *via* a single-channel pulse-height analyser to a separate counter. Thus we measure in a single scan the rocking curves of a series of planes of the same family each at a different wavelength. Data analysis in this case is simpler since all recorded rays (regardless of wavelength) traverse the same physical path so that the values of t_1 and t_2, calculated by fitting (5) to the data set whose F_h is known, are common to *all* the other rocking curves that are measured simultaneously with it. This procedure also minimizes the influence of possible sources of error like residual drifts, small nonlinearities in the scan *etc.*, since these influence all data sets equally, leaving the ratios of the corresponding structure factors unchanged. For these reasons, as well as the large reduction in the time required for data collection, this method is much preferable to the first procedure discussed above.

The computer programs developed for data analysis are based on a nonlinear corrected Gauss Newton iterative least-squares fitting procedure (NAG Subroutine Library, 1981; Gill & Murray, 1978). As the absolute intensity of the beam, I_0 of (5), is not known, the fitting program normalizes the data dynamically so as to obtain the best fit. Thus, for the characteristic radiation data the number of parameters optimized is usually four: F_h, t_1, t_2 and the intensity normalization factor. In a few cases the four-parameter fit indicated the presence of a small amount of constant background in the data. In those cases the run was repeated with the (constant) background as a fifth parameter to be optimized. Such cases were, however, very rare owing to the good collimation and the high-energy resolution of the solid-state detector, which reduced spurious background to below 0·002 counts s^{-1} in the measurement channels, compared with peak intensities of 100 counts s^{-1} with the continuous spectrum and several 1000 counts s^{-1} with characteristic radiation.

In the energy-dispersive mode three parameters were optimized by the fitting program. They are: F_h, the intensity normalization constant and the ratio of intensities of the π- and σ-polarized components of the primary beam. The inclusion of the last parameter in the fit was dictated by the energy-dependent partial polarization of the continuous spectrum of the tungsten tube (Compton & Allison, 1935). Core requirements of the program depend on the number of data points and the angular region scanned. A typical run used a core of 50 K words and required about 20 min of CPU time on a CDC 7600 computer. Convergence was very good, with a mean standard deviation well below 0·1% for all parameters and a residual sum of squares smaller than the sum of square roots of the data points.

3. Experimental

The monolithic diffractometer used in this study was cut from a perfect silicon single crystal with the (111) planes perpendicular to both the wafer faces and its base to better than 1′. Both wafers were nominally 275 μm thick and the overall dimensions of the monolith were 31 × 31 × 25 mm. Pinhole collimation to 10′ was used in the primary beam, and another pinhole was used to prevent spuriously reflected rays from reaching the detector. The finite divergence of the beam resulted in an energy resolultion $\delta E/E <$ 0·5% when working in the energy-dispersive mode. Computer simulations were carried out to check the influence of such energy smearing on the shape of the rocking curve and on the value of F_h deduced from it. It was found that the change in the calculated value of F_h on increasing $\delta E/E$ from 0 to 0·8% was less than 0·02%. Similar conclusions were drawn by Bonse, Graeff, Teworte & Rauch (1977). The signal-averaged (Hart & Siddons, 1981) data were collected under microcomputer control (Rodrigues & Siddons, 1979). The computer also drove the electromagnet through a 12 bit digital-to-analogue converter (DAC). The Ge solid-state detector used in this experiment fed a single counter *via* a single-channel pulse-height analyser (SCA) in the characteristic radiation mode and an array of up to six counters, each with its own SCA, when working in the energy-dispersive mode.

A polystyrene-foam enclosure surrounded by two metallic ones shielded the diffractometer from room-temperature fluctuations. The temperature was monitored by the computer and changed by less than 0·1 K during a 12 h data run. The mean temperature measured for each data set was used to adjust the value obtained for F_h to a common temperature of 293·2 K.

4. Results and discussion

A sum of five 12 h data runs collected in the energy dispersive mode with the 555 plane reflecting the Mo $K\bar{\alpha}$ wavelength is shown in Fig. 2. The rocking curves are completely symmetric within the statistical accuracy of the data and the contrast is also very high as evidenced by the sharp extrema straddling the central peaks of the 777 and 888 reflections, all of which indicate the absence of drifts. The very fast decrease in the rocking-curve width on increasing the order of the plane and the available dynamic range of the DAC limit the number of planes measurable in detail simultaneously. The step size for the data of Fig. 2 was adjusted to give ample resolution on the 888 and 777 reflection curves. Consequently, the 4096 steps available in a 12-bit DAC enabled us to measure only a small central portion of the rocking curve of the lowest-order plane in Fig. 2, the 444 plane. This, in turn, results in a somewhat poorer convergence of the fitting program as reflected in the slightly larger mean standard deviation quoted for 444 in Table 1. For the highest-order planes, the 999 and the 11,11,11, on the other hand, the limit $t/\Delta_0 \gg 1$ is reached and, as discussed in § 2, a structureless rocking curve results. The *Pendellösung* contrast for these planes is, thus, insufficient to ensure proper convergence of the fitting program, and no F_h values can be deduced from the data. In order to obtain useful data for these planes it would be necessary to work at a considerably higher Bragg angle, *i.e.* much longer wavelengths or thicker wafers. Both possibilities result in a prohibitively low intensity when using conventional sealed X-ray tubes, and would require the use of a synchrotron-radiation source. Preliminary data runs carried out at the Daresbury Laboratory Synchrotron Radiation Source indicated that an increase in intensity of three to four orders of magnitude can be obtained in these experiments. Further work is currently in progress.

Table 1. *Comparison of experimental and theoretical values of* F_h *(electrons).*

The first and third experimental structure factors were measured in the energy-dispersive mode and the second with Mo $K\bar{\alpha}$ characteristic radiation. Note that the theoretical values are consistently lower than the experimental ones.

Plane	Wavelength (Å)	$F_{h\,exp}$	$F_{h\,theor}$
444	0·8884	4·2437 (93)	4·2082
777	0·7107	1·3283 (42)	1·3239
777	0·5076	1·3053 (34)	1·3022

Fig. 3(*a*) shows the fit of the theoretical curve, (5), to the 555 rocking curve of a single data scan included in Fig. 2. The fit is excellent as demonstrated by the fact that the residuals, plotted in Fig. 3(*b*), are well within the limits of two standard deviations of the data and are randomly distributed. The same rocking curve, taken with characteristic Mo $K\bar{\alpha}$ radiation,

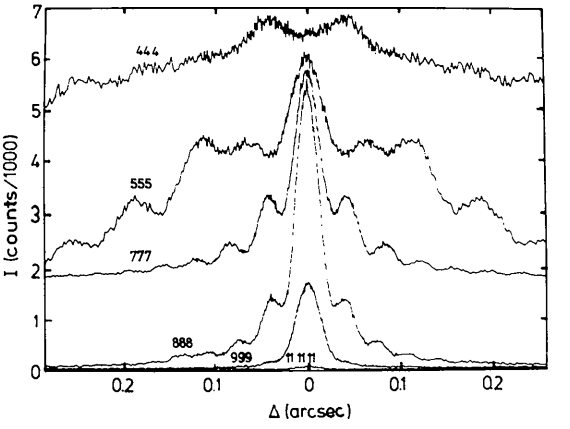

Fig. 2. A family of *hhh* rocking curves measured simultaneously in the energy-dispersive mode. The plot is the sum of five data sets. Note the large decrease in width as the order of the plane increases. The 444, 555 and 777 curves were shifted upwards in the plot by 200, 1000 and 1800 counts, respectively.

over twice the angular range of Fig. 2, is given in Fig. 4. The beam in these two cases hits the wafers at different points and the small 1·5% difference in the effective thicknesses of the wafers between the two spots is responsible for the change in shape, which is most pronounced in the neighbourhood of the central peak. This clearly demonstrates the sensitivity of the shape of the curve to the exact values of the wafer thicknesses and the difficulties which are apparent if local wafer thicknesses were to be measured in any other way.

Fits like the one given in Fig. 3 were carried out for five different sets of data and the five pairs of t_1 and t_2 thus obtained were used in fitting the theoretical curve to the 444 and the 777 rocking curves in the same data sets. Such a fit to the 777 rocking curve is given in Fig. 5. The high symmetry of the patterns enables us to identify spurious structure resulting from simultaneous reflections, or any other source. Such a structure can be seen in Fig. 5, 0·15″ to the left of the central peak. Its absence from the same position to the right of the peak identifies it as being spurious. Note that, since the complete curve is fitted, the presence of spurious structure confined to a small angular range does not impair the quality of the fit, as evidenced by the close fit between theory and experiment over the rest of the angular range plotted in Fig. 5.

The values of F_h calculated from some of the data included in Fig. 2 are listed in Table 1. A value of F_h for the 777 reflection obtained using Mo $K\bar{\alpha}$ characteristic radiation is also listed. In all cases, the standard deviations quoted refer to the mean of the values obtained from five different data sets, taking into account the standard deviation of the individual F_h values as obtained from the fitting program. The

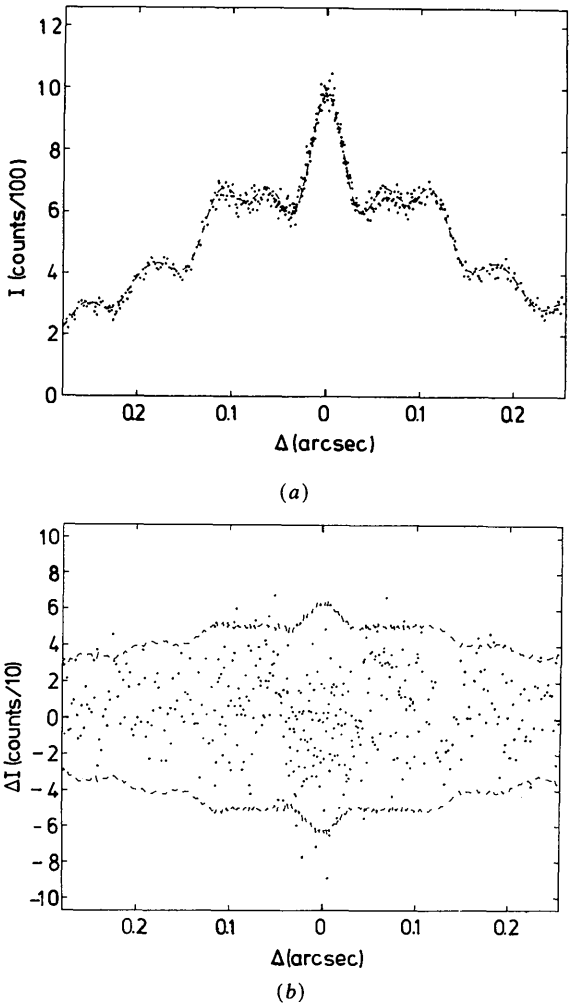

Fig. 3. The 555 rocking curve from a single data set included in Fig. 2. (*a*) The experimental (dots) and the fitted theoretical (broken line) curves for $F_{555}=2{\cdot}863$, $t_1=264{\cdot}63$ (0·11) μm and $t_2=277{\cdot}80$ (0·062) μm. Note the good fit and the high symmetry of the measured curve. (*b*) Fit residuals. The differences between theory and experimental (dots) are randomly distributed and well within the statistical 2σ level of the data (broken line).

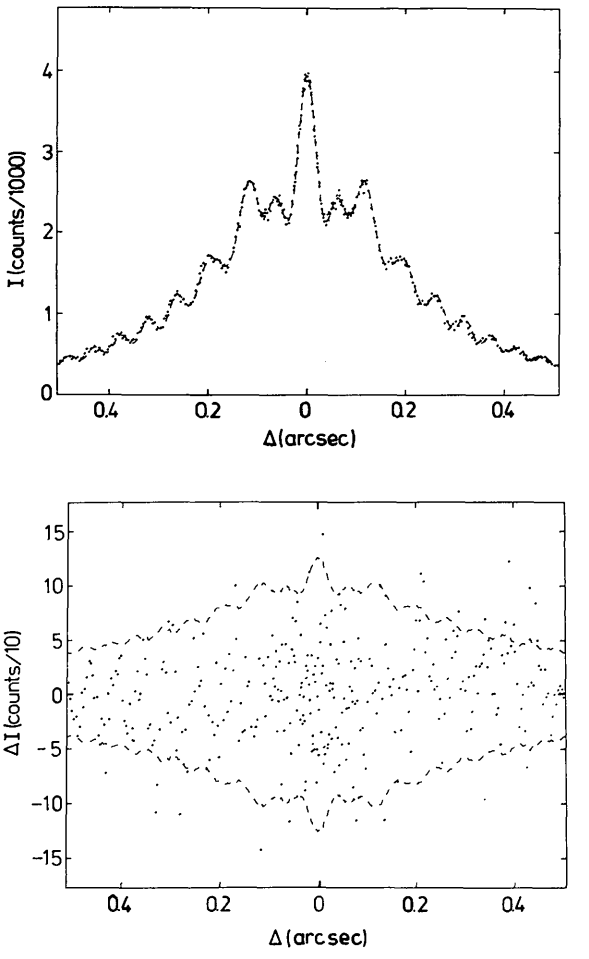

Fig. 4. The 555 rocking curve measured with characteristic Mo $K\bar{\alpha}$ radiation. Same notation as Fig. 3. $F_{555}=2{\cdot}847$, $t_1=273{\cdot}59$ (0·023) μm and $t_2=263{\cdot}73$ (0·078) μm.

magnitude of the individual standard deviations depends on the number of counts for each point and the amount of structure present in the data. No experimental value of F_{777} of comparable accuracy exists, and all published high accuracy values of F_{444} were measured at wavelengths different from ours. The F_{444} of Aldred & Hart (1973*a*) extrapolated, for dispersion, to the present wavelength is in excellent agreement with our value.

For the planes and accuracies quoted in Table 1, the structure factor can be approximated by (Aldred & Hart, 1973*a*, *b*)

$$F_h = 8a_g \exp[-B(\sin\theta_B/\lambda)^2](f+f'), \qquad (6)$$

where $B = -0{\cdot}4680$ (Price, Maslen & Mair, 1979) is the Debye parameter in the harmonic approximation, f is the atomic scattering factor and f' is the dispersion correction for the wavelength used. The theoretical values listed in Table 1 were calculated using relativistic Hartree-Fock f values (*International Tables for X-ray Crystallography*, 1974) and dispersion corrections calculated using the Cromer & Liberman (1970, 1981) method. Our measured values are consistently higher than the theoretical ones, particularly at low energies; thus corroborating Aldred & Hart's (1973*a*, *b*) conclusion that the Cromer & Liberman f' values are too low. A complete analysis and discussion of the present as well as additional data collected using the method presented here will be published in due course.

The method presented here, especially in the energy-dispersive mode, has the stability and accuracy required for deducing structure factors with a sub-0·1% accuracy even for high-order Bragg planes. This opens the way to a detailed study of the electron distribution in perfect crystals at both low and very high momentum transfer values, including bonding, anharmonic and core-electron relativistic effects. Since the monolithic diffractometer can be used over a wide temperature and pressure range, because independent calibration of the current/angle characteristic is no longer required, this new method has many potential applications in studies of bonding, temperature variation of scattering amplitudes and of anharmonicity.

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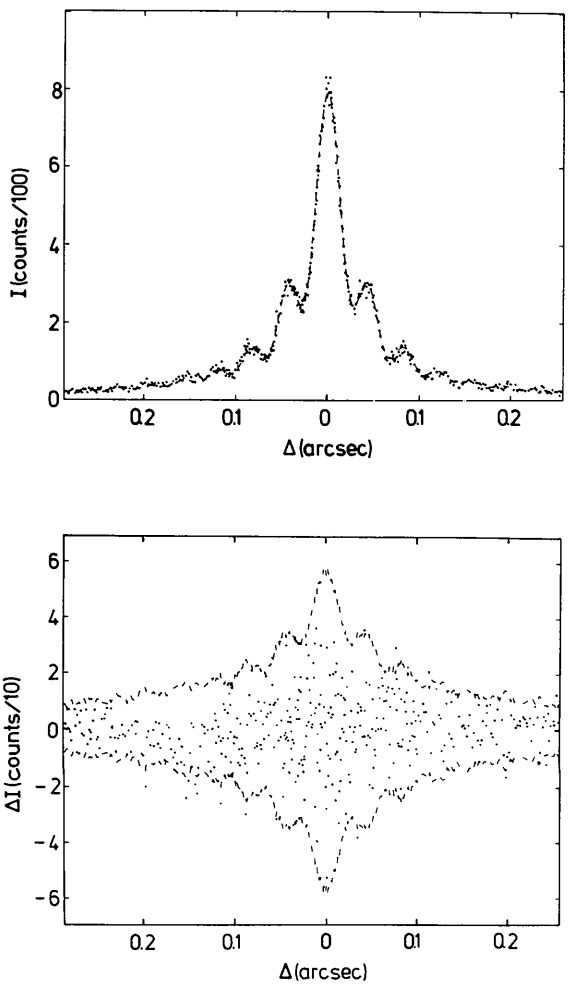

Fig. 5. The 777 rocking curve from a single data set included in Fig. 2. See caption of Fig. 3 for notation. $F_{777} = 1{\cdot}3024$, $t_1 = 264{\cdot}63\ (0{\cdot}11)$ μm and $t_2 = 277{\cdot}80\ (0{\cdot}062)$ μm.

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Exact Random-Walk Models in Crystallographic Statistics. II. The Bicentric Distribution for the Space Group $P\bar{1}$

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Abstract

An exact probability density function for the magnitude of the normalized structure factor $|E|$ has been derived for the space group $P\bar{1}$, taking account of the presence of one non-crystallographic center of symmetry. The function is based on the exact solution of the corresponding random-walk model and its expansion into a Fourier series. The above result is compared with simulated semi-cumulative distributions based on hypothetical structures and very good agreement is obtained for the equal-atom case, as well as for a heterogeneous asymmetric subunit containing fourteen carbon atoms and one uranium atom. The new exact bicentric probability density functions of $|E|$, for the space group $P\bar{1}$, reduce to the well known asymptotic expressions that are valid for equal-atom structures and a large number of atoms in the asymmetric unit of the space group.

Introduction

Effects of non-crystallographic symmetry on distributions of diffracted intensity have long since been recognized and investigated. Major attention has been devoted to the presence of one or more non-crystallographic centers in centrosymmetric (Lipson & Woolfson, 1952; Rogers & Wilson, 1953) and non-centrosymmetric (Srinivasan & Parthasarathy, 1976) crystals composed of equal atoms, and similar approximations based on the central limit theorem were also derived for the presence of non-crystallographic translational symmetry (hyperparallelism; Rogers & Wilson, 1953).

The best known, among these 'anomalous' distributions, is that due to the presence of one non-crystallographic center of symmetry, *i.e.* the bicentric distribution. An approximate generalization of this distribution to centrosymmetric space groups, and any atomic composition of the asymmetric unit, has recently been given by Ghosh & Nigam (1983) as a three-term expansion, with coefficients depending on definite integrals that can be tabulated. Another route to such generalizations has been outlined by Shmueli & Wilson (1982, 1983) and explicit polynomials, orthogonal to the Rogers-Wilson (1953) bicentric probability density function (p.d.f.) have been obtained. Such approximate generalizations may prove useful for not too large departures from the asymptotic bicentric p.d.f., but their convergence behavior is obviously space-group dependent and may give rise to difficulties in space groups of low symmetry (see, *e.g.*, Shmueli, 1982*a*).

An exact solution to this problem, at least for the important case of the space group $P\bar{1}$, can be given in the form of a p.d.f. based on a Fourier expansion of the exact solution to the problem of random walk (Barakat, 1974; Weiss & Kiefer, 1983; Kiefer & Weiss, 1984). Such p.d.f.'s have recently been applied with success to effects of atomic heterogeneity on departures from the widely used Wilson (1949) distributions (Shmueli, Weiss, Kiefer & Wilson, 1984).

The aims of the present paper are (i) to derive an exact probability density function for the magnitude of the normalized structure factor, which accounts for the presence of a non-crystallographic center in the asymmetric unit of $P\bar{1}$ for an arbitrary atomic composition, and (ii) to demonstrate the probable

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