Short Communications

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Acta Cryst. (1974). A**30**, 600

A determination of the absolute values and signs of the 111 and 222 structure factors of silicon.

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(*Received* 16 *January* 1974; *accepted* 12 *March* 1974)

The thickness fringes of a silicon wedge at the Bragg positions for 111 and 222, and at the symmetric position for *hhh* were observed with the electron microscope at 100 and 392 kV. The ratios of the measured fringe distances were analysed by the many-beam dynamical theory in electron diffraction assuming the theoretical values for the structure factors of orders higher than 333. As the result, the crystal structure factors are derived as $F_{111}=59{\cdot}87\pm0{\cdot}46$ and $F_{222}=-1{\cdot}85\pm0{\cdot}85$ at 293°K.

The structure factors of silicon have been extensively studied by the X-ray intensity measurement (Göttlicher & Wölfel, 1959; DeMarco & Weiss, 1965) and the X-ray dynamical methods (Hattori, Kuriyama, Katagawa & Kato, 1965; Tanemura & Kato, 1972; Aldread & Hart, 1973). The 222 structure factor, which should vanish for spherically symmetric atoms, was found to be about 2% of that for 111. However, the sign has not yet been determined directly by any X-ray diffraction methods, although Dawson (1967) calculated it by a theoretical analysis. With electron diffraction methods on the basis of the many-beam dynamical theory as adopted by Cowley (1969) and Kreutle & Meyer-Ehmsen (1971), the sign can also be determined in principle. In the present work, both the absolute value and sign were determined on the same principle but with a different experimental technique.

A parallel $\{11\bar{1}\}$ plate of silicon was thinned to less than 0·1 mm and the surfaces were chemically polished. Then, it was fractured by a knife resulting in a wedge form with nearly a right angle bounded by one of the polished surfaces and the fracture plane. The specimen was mounted on the tilting stage of an electron microscope so that the (111) plane could be nearly parallel to the incident beam. This permitted easy access to the symmetric position, where the beam was perfectly parallel to the (111) plane, and to the 111 and 222 Bragg conditions, taking care to avoid accidental reflexions. The thickness fringes of the wedge at each orientation were taken in the bright and dark fields at 100 and 392 kV. The distances of the fringes l_{111}, l_{222} and l_{000} were measured, where l_{000} denotes that at the symmetric position. The ratios $R_{0,1}=l_{000}/l_{111}$, $R_{0,2}=l_{000}/l_{222}$ and $R_{1,2}=l_{111}/l_{222}$ listed in Table 1 were analysed by the first method which was proposed previously (Ichimiya, Arii, Uyeda & Fukuhara, 1973).

Table 1. *Measured ratios of the fringe distances*

	$R_{0,1}$	$R_{0,2}$	$R_{1,2}$
100 kV	0·503 ± 0·007	0·220 ± 0·008	0·435 ± 0·015
392 kV	0·542 ± 0·004	0·329 ± 0·003	0·607 ± 0·008

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According to the dynamical theory of electron diffraction, the ratio of the fringe distances can be expressed as

$$R_{h,k}=R_{h,k}(E, V_{111}, V_{222}, V_{333}, \ldots)\,, \qquad (1)$$

where the function $R_{h,k}$ is given by solving the secular equation for the many-beam case, E is the accelerating voltage and the V_{hhh}'s are the *hhh*th Fourier coefficients of the crystal potential. Since the theoretical values of V_{hhh} are supposed to be accurate provided that the order *hhh* is higher than 333, the values calculated from the theoretical X-ray atomic scattering factors (Cromer & Mann, 1968) were employed. In the present analysis, therefore, V_{111} and V_{222} are regarded as unknown variables. In the practical calculation, 15 systematic beams were taken into account.

Using each experimental ratio in equation (1), a curve can be drawn on the V_{111}–V_{222} diagram. Three curves are obtained from the three ratios as shown in Fig. 1. From the intersecting region of the three curves, the coefficients V_{111} and V_{222} are determined as listed in Table 2. The accuracy is higher for 392 kV than for 100 kV, because the number of the fringes is larger at the higher voltage.

Table 2. *Fourier coefficients of the crystal potential of silicon at* 293°K (V)

	V_{111}	V_{222}
100 kV	5·13 ± 0·20	0·12 ± 0·08
392 kV	5·19 ± 0·11	0·14 ± 0·05
Weighted mean	5·18 ± 0·13	0·13 ± 0·06

The crystal structure factor at room temperature, F_{hkl}, is calculated from the V_{hkl} obtained by experiment as follows

$$F_{hkl}=Z\,.\,S_{hkl}\,.\exp\left\{-B\left(\frac{\sin\theta}{\lambda}\right)^2\right\} - \frac{\pi a_0(h^2+k^2+l^2)}{e}\cdot\frac{V_{hkl}}{300}\,, \qquad (2)$$

where Z is the atomic number, $\exp\{-B(\sin\theta/\lambda)^2\}$ the Debye–Waller factor, a_0 the lattice constant, and e the electronic charge. The value of V_{hkl} is given in volts and the denominator 300 is necessary for the conversion of the units. The geometrical factor S_{hkl} is $4\sqrt{2}$ for 111 and zero

for 222. By using the temperature factor $B=0.46$ Å^2 (at 293°K) obtained by Aldread & Hart (1973), the crystal structure factors including the sign are calculated to be $F_{111}=59.87\pm0.46$ and $F_{222}=-1.85\pm0.85$ at 293°K. The present value of F_{111} is smaller by about 1% compared to the most accurate data from X-rays (Tanemura & Kato, 1972; Aldread & Hart, 1973), whereas that of F_{222}, which is due to the antisymmetric part of the charge distribution (Dawson, 1967), is larger than all the available data as seen in Table 3.

Table 3. *The structure factors F_{111} and F_{222} at room temperature converted from the original data*

Source	Method	F_{111}	F_{222}
G. & W. (1959)	X-ray Int.	60·81 ± 0·11	1·12 ± ? *
D. & W. (1965)	X-ray Int.	60·47 ± 0·45	1·44 ± 0·08*
H.K.K.K. (1965)	X-ray Dyn.	62·12 ± 0·93	−1·44 ± 0·08†
T. & K. (1972)	X-ray Dyn.	60·32 ± 0·01	
A. & H. (1973)	X-ray Dyn.	60·32 ± 0·03	−1·35 ± 0·04†
Cowley (1969)	Electr. Dyn.	60·36 ± ?	−0·07 ± ?
K. & M. (1971)	Electr. Dyn.	59·97 ± 0·05	−1·6 ± 0·2
Present (1974)	Electr. Dyn.	59·87 ± 0·46	−1·85 ± 0·85

* The sign has not been determined.
† Theoretical values calculated by Dawson's (1967) formula.

In the above analysis, it was shown that the sign of the structure factor for centrosymmetric crystals can be determined by electron-dynamical methods by taking account of many-beam effects. Cowley's (1969) method is similar to the present one, but it does not seem adequate for accurate determination. Although Kreutle & Meyer-Ehmsen's (1971) method gives high accuracy, a highly refined technique of intensity measurement is required. On the other hand, the present method needs only the measurement of the fringe spacings in the electron micrographs. By a similar method, one of the present authors has recently determined the phase angle of the structure factor for the 0002 reflexion in cadmium sulphide, which has no centre of symmetry. Details of the experiments for silicon and cadmium sulphide will be published elsewhere in the near future.

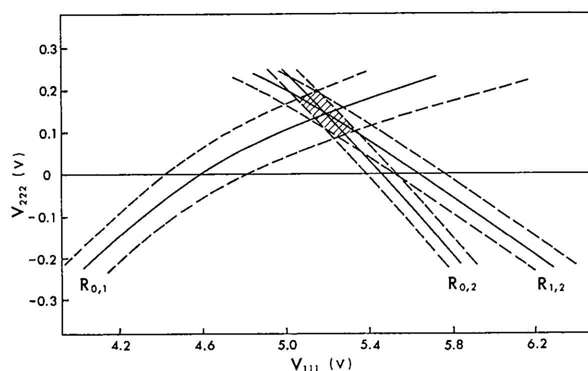

Fig. 1. Determination of V_{111} and V_{222} of silicon at 392 kV. The ratios of the fringe distances $R_{0,1}$, $R_{0,2}$ and $R_{1,2}$ are listed in Table 1. A pair of broken lines are drawn corresponding to the errors of each ratio.

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Acta Cryst. (1974). A**30**, 601

Treatment of negative indices in crystallographic fast Fourier transforms. By P. R. MALLINSON,* *Molecular Structures Department, Rothamsted Experimental Station, Inveresk House,* 346 *Strand, London WC2R OHG, England* and F. N. TESKEY, *Clare College, Cambridge, England*

(*Received* 27 *November* 1973; *accepted* 26 *March* 1974)

An algorithm for fast Fourier transformation using sequentially organized backing storage is described; a simple modification has been made to an existing procedure, to allow the Fourier coefficients to have negative indices, without the need to introduce additional phase factors. A general purpose crystallographic FFT program has been written for a 16K IBM 1130 with three disks.

There has been some interest in applying the fast Fourier transform (FFT) to crystallography since its discovery by Cooley & Tukey (1965). Methods have been described for incorporating the space-group symmetry (Ten Eyck, 1973), and for using backing store to accommodate the array of data (Singleton, 1967; Lange, Stolle & Huttner, 1973). The general formula is

$$\varrho(x,y,z)=\sum_{h=h_a}^{h_e}\sum_{k=k_a}^{k_e}\sum_{l=l_a}^{l_e}F_{hkl}\exp -2\pi i\varphi$$

where

$$\varphi=hx/N+ky/O+lzP \qquad (1)$$

$$N=h_e-h_a;\quad O=k_e-k_a;\quad P=l_e-l_a;$$

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