PACK, R. T. & BROWN, W. B. (1966). *J. Chem. Phys.* **45**, 556–559.

PRICE, P. F., MASLEN, E. N. & MAIR, S. L. (1978). *Acta Cryst.* A**34**, 183–193.

PRICE, P. F., MASLEN, E. N. & MOORE, F. H. (1978). *Acta Cryst.* A**34**, 171–172.

PRICE, P. F., VARGHESE, J. N. & MASLEN, E. N. (1978). *Acta Cryst.* A**34**, 203–216.

STEWART, R. F. (1972*a*). *Electron Population Analysis with Generalized X-ray Scattering Factors*. Unpublished.

STEWART, R. F. (1972*b*). *J. Chem. Phys.* **57**, 1664–1668.

STEWART, R. F. (1973*a*). *J. Chem. Phys.* **58**, 1668–1676.

STEWART, R. F. (1973*b*). *Acta Cryst.* A**29**, 602–605.

STEWART, R. F. (1973*c*). *J. Chem. Phys.* **58**, 4430–4438.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

SYGUSCH, J. (1974). *Crystallographic Studies of Two Antibiotics and of Diglycolic Acid. Experimental Charge Density Analysis of Diglycolic Anhydride.* Thesis, Univ. Montreal.

WATSON, G. N. (1952). *Theory of Bessel Functions*, p. 394. Cambridge Univ. Press.

WITH, G. DE & FELL, D. (1975). *Chem. Phys. Lett.* **30**, 279–283.

YANG, Y. W. (1975). Private communication.

Acta Cryst. (1978). A**34**, 183–193

Electron-Density Studies.
III. A Re-evaluation of the Electron Distribution in Crystalline Silicon

BY P. F. PRICE AND E. N. MASLEN

Department of Physics, University of Western Australia, Nedlands, Western Australia

AND S. L. MAIR

Division of Chemical Physics, CSIRO, PO Box 160, Clayton, Victoria, Australia 3168

(*Received 13 December* 1976; *accepted* 23 *February* 1977)

Highly accurate absolute measurements of the X-ray structure factors of silicon [Aldred & Hart, *Proc. R. Soc. London, Ser. A*, (1973), **332**, 223–238] have been used to analyse a number of models for the electron distribution. Initially, the valence-electron distribution (with the neon core assumed to be unmodified from that of the isolated silicon atoms) was built up with a radial basis of the form $r^n \exp(-\zeta r)$ and non-sphericity was allowed for by inclusion of octupole and hexadecapole terms. Improved representation was achieved with related models in which deformations from the total isolated-atom electron density were refined instead. The exact shape of the deformation electron density in the region of the bond was sensitively dependent on the monopole deformation term. The anomalous-dispersion contributions ($\Delta f'$) to the scattering factors were refined and found to be in agreement with recent interferometric measurements, but not with recent calculations. The octupole density term is slightly sharper at 293·2 than at 92·2 K, and the structure factor for the 222 reflection is predicted to be larger at the higher temperature. These effects may be due to a failure of the convolution approximation or to uncertainties in the anharmonic corrections to the structure-factor data.

Introduction

The one-electron density of a molecular system is a fundamental observable (Hohenberg & Kohn, 1964) which, in principle, can be measured by coherent X-ray scattering. The qualitative description of a molecule as a sum of deformed atoms (or 'pseudo-atoms') has long been popular in chemistry, and recent work by Bader and co-workers (see, for example, Srebrenik & Bader, 1975) indicates that this viewpoint may have a more rigorous basis in that the properties of a system may be expressible in terms of those of its component density fragments.

A variety of pseudo-atom definitions have been proposed for the analysis of X-ray diffraction data (Dawson, 1967*a*; Kurki-Suonio & Ruuskanen, 1971; Hirshfeld, 1971; Stewart, 1972, 1973*a*; Sygusch, 1974). The essential differences were discussed in a previous paper [Price & Maslen (1978), hereinafter referred to as paper II]. It was shown there that in the analysis of powdered-diamond diffraction data most of the models resulted in similar fits to the data (R and R_w factors of approximately 0·01, and a GoF of near 3)* and gave similar descriptions of broad charge-density features, but differed in their determinations of the Debye–Waller B value. Several of the models have been useful in the description of the electron density in crystals of small organic molecules containing first-row atoms and hydrogen (Hirshfeld, 1971; Harel & Hirshfeld, 1975; Harel, Hecht & Hirshfeld, 1975; Berkovitch-Yellin & Leiserowitz, 1975; Price, Varghese & Maslen, 1978, paper V). Their suitability for structures containing second-row atoms or transition metals has not been tested.

Just as diamond, with valence electrons belonging to the L-shell, might reasonably be regarded as a prototype for valence-density models intended for use with first-row atoms, the silicon electron density serves as a reference for the study of the M-shell valence distribution to be found in second-row atoms. Apart from the analysis of Aldred & Hart (1973*b*, see below), previous analyses of the electron density in silicon (Dawson, 1967*b*; McConnell & Sanger, 1970; Kurki-Suonio & Ruuskanen, 1971) were based on structure factors of precision 0·5% at best (see also Dawson, 1975).

The *Pendellösung* data of Aldred & Hart (1973*a*) are of accuracy better than 0·2%. These data consist of measurements of the absolute structure factors of crystalline silicon out to Miller indices of 8,8,0 (with some reflections excluded) collected at 92·2 and 293·2 K with Mo $K\alpha_1$ and Ag $K\alpha_1$ radiations.

Aldred & Hart (1973*b*) analysed their data in terms of an electron-density model similar to that proposed by Dawson (1967*b*), except for a '6·8% expansion of the valence shell'. This model, in the notation of paper II, represents the thermally-averaged deformation density with octupole and hexadecapole terms of Gaussian radial dependence with radial order 2 and exponent fixed at the value (0·88 Å^{-2}) suggested by Dawson (1967*b*). The expansion of the valence shell was parametrized by using a monopole deformation term of the form

$$\Delta f(s,\varepsilon) = [f_{\rm Si}(s_\varepsilon) - f_{{\rm Si}^{4+}}(s_\varepsilon)] - [f_{\rm Si}(s) - f_{{\rm Si}^{4+}}(s)],$$

where s is $\sin\theta/\lambda$, $s_\varepsilon = s(1-\varepsilon)$ and $f_{\rm Si}(s)$ and $f_{{\rm Si}^{4+}}(s)$ are the scattering factors of the isolated atom and the ion taken from the *International Tables for X-ray Crystallography* (1962). The parameter ε was determined to be 0·068 and this 6·8% contraction of the valence-shell scattering factor was described as a 6·8% expansion of the valence shell.

In their analysis Aldred & Hart (1973*b*) used the dispersion corrections $\Delta f'_{\rm Mo} = 0{\cdot}090$ and $\Delta f'_{\rm Ag} = 0{\cdot}060$ for Mo $K\alpha_1$ and Ag $K\alpha_1$ radiation respectively (Cromer, 1965), but concluded that these should be increased slightly to $\Delta f'_{\rm Mo} = 0{\cdot}103$ and $\Delta f'_{\rm Ag} = 0{\cdot}073$.

After correction for anomalous dispersion and the different temperature factors, Aldred & Hart (1973*b*) considered the four data sets to be identical within the errors. Their final R factor, for the averaged data, was 0·0014. Although this is small by crystallographic standards it is higher than is expected from the quoted experimental errors in the measurements. Their calculated structure factor (per atom) for the 'forbidden' 222 reflection at room temperature is $-0{\cdot}169 \pm 0{\cdot}005$, which is somewhat below most of the direct experimental results (see Table 6).

In this paper we re-analyse Aldred & Hart's (1973*a*) data, firstly in terms of an at-rest valence-density model and then in terms of an at-rest deformation-density model. The pseudo-atom density functions chosen have the angular dependence of the surface harmonics (multipoles) and exponential radial functions with optimized exponents, as in paper II. The multipole expansion is limited to the hexadecapole (fourth-order) level.

Thermal motion

We assume initially that the convolution approximation (or rigid-ion model) is valid. The atomic scattering factor is then multiplied by a temperature factor which is the Fourier transform of the nuclear smearing function.

The temperature factor arises from both harmonic and anharmonic components of the atomic vibrations. The dominant anharmonic effect is expected to be due to the cubic term in the 'effective one-particle potential' (Dawson, Hurley & Maslen, 1967). The data of Aldred & Hart (1973*b*) do not go out to sufficiently high angles to determine accurately the cubic force constant, so that it was necessary to apply an anharmonic correction to the structure factors before investigating the charge-density information. Roberto, Batterman & Keating (1974) have estimated the cubic anharmonic force constant from neutron-diffraction measurements of the 222 reflection as $\beta = 5{\cdot}42 \times 10^{-12}$ erg Å^{-3} at room temperature. The expression which they used for the anharmonic temperature factor is the high-temperature limit of that given by Dawson & Willis (1967), *i.e.* the Debye–Waller factor, B, in the latter is replaced by $8\pi^2kT/\alpha$, where α has a constant value of $7{\cdot}85 \times 10^{-12}$ erg Å^{-2} and k is the Boltzmann constant. Because of a fortuitous near-cancellation of terms, the expression used by Roberto *et al* (1974) gives the quantum-corrected value for β at room temperature to

---

* Agreement factors R and R_w are defined as

$$R = \Sigma|\Delta F_i|/\Sigma|F_{i,\,\rm obs}|$$
$$R_w = [(\Sigma\, w_i \Delta F_i^2/\Sigma\, w_i F_{i,\,\rm obs}^2)]^{1/2}$$

and the goodness of fit parameter (GoF) as

$$\mathrm{GoF} = [\Sigma\, w_i \Delta F_i^2/(n-m)]^{1/2},$$

where ΔF_i is the difference between the observed, $F_{i,\,\rm obs}$, and calculated, $F_{i,\,\rm calc}$, structure factors, w_i is the weight of the ith structure factor, n is the number of observed structure factors and m is the number of parameters.

a very good approximation (see Mair & Wilkins, 1976). Even at 92·2 K, the above high-temperature approximation is sufficiently good to allow correction of the data of Aldred & Hart (1973*b*) for anharmonic effects without incurring significant error, assuming that the effective one-particle potential model is still applicable. The corrections were applied with the above value of β used at both temperatures. The effect on the structure factors was found to be less than their standard deviations in all cases except for the 555 reflection at room temperature.

The Debye–Waller B value, which is constrained to be isotropic by the site symmetry, was included as a parameter in the analysis. As discussed in paper II, the omission of monopole terms from the deformation-density model may cause the determined B value to be in error. When monopole terms with adjustable amplitudes are included in the charge-density model, the resulting high correlation between the amplitudes and the B value precludes their simultaneous determination. Since there is no accurate, independent measurement of the B value we are forced to determine it from the data. The amount by which it will be in error will depend on the errors in the atomic core density and in the anomalous dispersion corrections, and on the amount of core deformation in the bonded system. Fortunately the last is expected to be small.

Following Aldred & Hart (1973*b*), the nuclear contribution to the structure factors was taken to be 0·004 electron units, and, initially, the anomalous dispersion corrections of Cromer (1965) were used. These were assumed to be diminished with scattering angle by the Debye–Waller factor.

The errors quoted in Table 3 of Aldred & Hart (1973*a*) were taken as estimated standard deviations (e.s.d.'s) in the structure factors, and weights were assigned to be the inverse squares of these e.s.d.'s.

Valence density

Stewart's (1972, 1973*a*) valence-density model has been useful in the description of the electron density in systems of first-row atoms and hydrogen (Stewart, 1973*b*; paper V). The neon-core density is calculated from the Hartree–Fock 1*s*, 2*s* and 2*p* orbitals of silicon as listed by Clementi (1965), each of which is populated with two electrons. The valence density is written as the sum of monopole, octupole and hexadecapole terms, of the form

$$\rho_0(\mathbf{r}) = P_{\rm val}[Z_V^{n_V+3}/(n_V+2)!]\,r^{n_V}\exp(-Z_V r)/4\pi \qquad (1)$$

$$\rho_3(\mathbf{r}) = O[Z_O^{n_O+3}/(n_O+2)!]\,r^{n_O}\exp(-Z_O r]\,[xyz/r^3] \qquad (2)$$

$$\rho_4(\mathbf{r}) = H[Z_H^{n_H+3}/(n_H+2)!]\,r^{n_H}\exp(-Z_H r) \times [160/(27\sqrt{3\pi})]\,[x^4+y^4+z^4-(3/5)r^4]/r^4. \qquad (3)$$

Symmetry and electroneutrality constrain $P_{\rm val}$ to equal 4 e. Following the usual practice, we initially constrain the exponents Z_V, Z_O and Z_H to be equal, and write this exponent as $2Z$. The radial orders were initially fixed at $n_V = 4$, $n_O = 3$, $n_H = 4$.

As in the analysis of diamond by Stewart (1973*b*), and in papers IV (Price, Maslen & Delaney, 1978) and V, we initially constrain the valence exponent to the standard molecular value (Hehre, Ditchfield, Stewart & Pople, 1970) of Z = 1·52 bohr^{-1}. In contrast to the cases of structures containing only first-row atoms (papers IV and V), in silicon there was a significant improvement in the fit to the data with the inclusion of the octupole and hexadecapole terms. The final GoF parameters were near the value 6.

The effect of exponent refinement was similar to that in the other analyses. At the 'scalars only' level of the model (*i.e.* refinement of the B value and the exponent, Z, with O and H constrained at zero) the exponent was not significantly different from the standard molecular value. Inclusion of the octupole term resulted in a significant improvement to the model and a decrease in the exponent to 1·49 (2)* bohr^{-1}. Subsequent addition of the hexadecapole resulted in a further improvement in the fit and an exponent of 1·48 (2) bohr^{-1}. These four parameter (B,Z,O,H) results for Aldred & Hart's (1973*b*) four data sets are shown in Table 1. For comparison purposes a refinement of the valence-density parameters was also made using as data the calculated structure factors for the isolated-atom situation [with Clementi's (1965) wavefunctions] and a B value of zero. The results are shown as 'data set 5'. The experimental e.s.d.'s for the structure factors of data set 5 were taken as the mean of those of data sets 1 to 4. The fit of the valence-density model to data set 5 is not good (GoF = 3·4, R = 0·0026), suggesting that our radial basis set could be improved. The B value of −0·025 (4) Å^2 suggests that the B values with the valence-density model will be some 0·025 Å^2 smaller than those using a simple deformation-density model. That this is indeed the case can be seen from the results of the next section.

The final refinement indices are GoF $\simeq$ 5, $R_w \simeq$ 0·004, $R \simeq$ 0·004, indicating that the fit to the data is much poorer than that obtained by Aldred & Hart (1973*b*) using the Dawson (1967*b*) model. Thus, the simple valence-density model, with its single exponential radial functions, is clearly inadequate to describe accurately the charge density and thermal motion in silicon. This conclusion was not altered by variation in the radial order of the multipole terms, by separate refinement of the multipole exponents or by allowing, through variation of the 2*s*, 2*p* and valence popuations, transfer of charge from the L shell to the M shell. This confirms an earlier observation by Allen-

---

* Least-squares parameter e.s.d.'s, multiplied by the GoF and expressed in the same units as the last significant figure, are enclosed in parentheses.

Table 1. *Silicon valence density model* ($B\ Z\ O\ H$ [3,4])

The orders of the octupole and hexadecapole radial functions were fixed at 3 and 4 respectively. All of the valence exponents were constrained to be equal. The fifth column contains the mean values, with the distribution e.s.d. in parentheses. The data set 5 analysis used 'experimental' structure factors calculated from the isolated atom approximation [with Clementi's (1965) wavefunctions] and a B value of zero.

	Data set 1 92·2 K Mo $K\alpha_1$	Data set 2 92·2 K Ag $K\alpha_1$	Data set 3 293·2 K Mo $K\alpha_1$	Data set 4 293·2 K Ag $K\alpha_1$	Mean	Data set 5 HF Clementi (1965)
B(Å^2)	0·205 (7)	0·202 (8)	0·436 (8)	0·439 (4)	0·204/0·438	−0·025 (4)
Z(bohr^{-1})	1·48 (2)	1·48 (2)	1·48 (1)	1·49 (2)	1·48 (1)	1·46 (1)
O(e)	0·23 (6)	0·26 (6)	0·32 (6)	0·17 (5)	0·25 (6)	0·05 (5)
H(e)	−0·13 (5)	−0·16 (5)	−0·21 (8)	−0·13 (5)	−0·16 (4)	0·00 (2)
$r_{m,3}$*	0·38 (1)	0·38 (1)	0·38 (0)	0·38 (1)	0·38 (0)	0·39 (0)
GoF	4·6	5·5	6·5	4·6	5·3 (9)	3·4
R_w	0·0045	0·0052	0·0019	0·0043	0·0040 (14)	0·0032
R	0·0042	0·0049	0·0053	0·0039	0·0046 (6)	0·0026
	Results from Aldred & Hart's (1973*b*) analysis†			B_{12} = 0·227 (3) B_{34} = 0·461 (3) R = 0·0014	O = 0·463 H = −0·175 $r_{m,3}$ = 0·64	

* The position of the maximum of the function $r^2\rho_3(\mathbf{r})$ is expressed as a fraction of the bond length. In this model it is largely determined from the shape of the monopole term.

† Aldred & Hart (1973*b*) used Gaussian radial functions, and constrained the Gaussian breadth parameter at Dawson's (1967*b*) value of 0·88 Å^{-2}.

Table 2. *Silicon deformation density* ($B\ O\ Z_O\ H$ [4,4])

The orders of both the octupole and hexadecapole radial functions were fixed at 4, and both exponents, Z_o and Z_H were constrained to be equal. The 222 structure factors (per atom), f_{222}, have been corrected for explicit thermal-motion effects.

	Data set 1	Data set 2	Data set 3	Data set 4	Mean
Temperature	92·2 K	92·2 K	293·2 K	293·2 K	
Radiation	Mo $K\alpha_1$	Ag $K\alpha_1$	Mo $K\alpha_1$	Ag $K\alpha_1$	
B(Å^2)	0·239 (7)	0·236 (6)	0·469 (5)	0·467 (4)	0·237 (2) 0·468^5 (1)
O(e)	0·33 (6)	0·35 (4)	0·32 (4)	0·31 (4)	0·326 (18)
Z_O(bohr^{-1})	2·66 (25)	2·73 (18)	2·71 (18)	2·70 (18)	2·70 (3)
H(e)	−0·08 (6)	−0·10 (5)	−0·07 (6)	−0·08 (4)	−0·084 (12)
$r_{m,3}$*	0·51 (5)	0·49 (3)	0·50 (3)	0·50 (3)	0·500 (6)
f_{222}	0·173	0·194	0·178	0·169	0·179 (11)
GoF	4·7	4·5	4·3	3·8	4·3 (4)
R_w	0·0046	0·0043	0·0013	0·0035	0·0034 (15)
R	0·0030	0·0030	0·0028	0·0025	0·0028 (2)

* The position of the maximum of the function $r^2\rho_3(\mathbf{r})$ is expressed as a fraction of the bond length.

Williams, Delaney, Furina, Maslen, O'Connor, Varghese & Yung (1974) that this type of model does not sample the density efficiently for second-row atoms.

Deformation density

Our next model for the charge density uses the isolated atom as a basis and represents deformations from this with functions similar to those used in the previous section. The isolated-atom scattering factors used were those of Doyle & Turner (1968). These proved slightly superior to the earlier values of Clementi (1965).

We start with the standard crystallographic charge-density model (isolated atom or zero-deformation density model) by refining only on the B value. The resulting refinement indices ($R \simeq 0{\cdot}007$, GoF $\simeq 10$) are a rough measure of the inadequacy of this model for the silicon structure.

Following the diamond analysis (paper II) we next include third and fourth-order terms as given by equations (2) and (3) with $n_O = n_H$ and $Z_O = Z_H$. The four adjustable parameters are B, O, Z_O and H. These results are shown in Table 2. The mean values are shown in the right-hand column. Numbers in brackets there relate to the estimated standard deviation, s_x, of the distribution of the values of x, where

$$s_x = \{[\Sigma(x-\bar{x})^2/(n-1)]\}^{1/2},$$

rather than to the e.s.d. of the mean ($s_{\bar{x}} = s_x/\sqrt{n}$). Following normal practice the parameter e.s.d.'s have been multiplied by the GoF to allow for the precision of the structure factor measurements.

The mean GoF is 4·3 (4) and mean R factor 0·0028 (2), both a little less than those of the valence-density analysis, but still reflecting opportunity for improvement. This model then, is also inadequate. Nevertheless it is interesting to compare the results

Table 3. *Silicon deformation density*

(*a*) $B\ PC\ Z\ O\ Z_O\ H$ [3,4]

The radial orders of the octupole and hexadecapole functions were fixed at 3 and 4 respectively. The exponents Z_O, Z_H were constrained to be equal. The 222 structure factors (per atom), f_{222}, have been corrected for explicit thermal motion effects.

	Data set 1	Data set 2	Data set 3	Data set 4	Mean*
Temperature	92·2 K	92·2 K	293·2 K	293·2 K	
Radiation	Mo $K\alpha_1$	Ag $K\alpha_1$	Mo $K\alpha_1$	Ag $K\alpha_1$	
B(Å^2)	0·2375 (13)	0·2338 (16)	0·4690 (10)	0·4671 (12)	0·2357 (26) 0·4681 (13)
PC(e)	0·38 (9)	0·30 (8)	0·35 (8)	0·20 (5)	0·34 (4)
Z(bohr^{-1})	2·21 (10)	2·30 (14)	2·18 (10)	2·53 (18)	2·23 (6)
O(e)	0·48 (6)	0·46 (6)	0·49 (5)	0·42 (4)	0·48 (2)
Z_O(bohr^{-1})	1·76 (6)	1·83 (7)	1·83 (6)	1·96 (7)	1·81 (4)
H(e)	−0·37 (4)	−0·31 (4)	−0·33 (4)	−0·19 (3)	−0·34 (3)
R†	0·56 (3)	0·54 (3)	0·57 (3)	0·49 (3)	0·553 (15)
$r_{m,3}$‡	0·64 (2)	0·61 (2)	0·61 (2)	0·54 (2)	0·623 (14)
f_{222}	0·145	0·150	0·161	0·167	0·152 (8)
GoF	0·76	0·91	0·69	1·13	0·79 (11)
R_w	0·0007	0·0008	0·0002	0·0010	0·0006 (3)
R	0·0006	0·0009	0·0005	0·0008	0·0007 (2)

(*b*) $B\ PC\ Z\ O\ Z_O\ H$ [4,4]

The radial orders of the octupole and hexadecapole functions were both constrained to be 4. The exponents Z_O, Z_H were constrained to be equal. The 222 structure factors (per atom) f_{222}, have been corrected for explicit thermal-motion effects.

	Data set 1	Data set 2	Data set 3	Data set 4	Mean*
Temperature	92·2 K	92·2 K	293·2 K	293·2 K	
Radiation	Mo $K\alpha_1$	Ag $K\alpha_1$	Mo $K\alpha_1$	Ag $K\alpha_1$	
B(Å^2)	0·2370 (13)	0·2335 (14)	0·4686 (11)	0·4666 (11)	0·2353 (25) 0·4676 (14)
PC(e)	0·31 (8)	0·24 (6)	0·27 (7)	0·16 (3)	0·27 (4)
Z(bohr^{-1})	2·25 (13)	2·36 (15)	2·24 (13)	2·66 (18)	2·28 (7)
O(e)	0·52 (6)	0·49 (5)	0·51 (5)	0·43	0·51 (2)
Z_O(bohr^{-1})	2·14 (7)	2·22 (6)	2·24 (6)	2·39 (6)	2·20 (5)
H(e)	−0·17 (2)	−0·15 (2)	−0·15 (2)	−0·10 (2)	−0·16 (1)
R†	0·55 (2)	0·52 (3)	0·55 (2)	0·46 (3)	0·540 (15)
$r_{m,3}$‡	0·63 (2)	0·61 (1)	0·56 (1)	0·614 (15)	
f_{222}	0·175	0·181	0·195	0·194	0·184 (10)
GoF	0·77	0·83	0·73	1·09	0·78 (5)
R_w	0·0007	0·0007	0·0002	0·0009	0·0005 (3)
R	0·0006	0·0008	0·0006	0·0008	0·0007 (1)

* Means of data sets 1–3 only.

† The position of the (central) zero of the function $\rho_0(\mathbf{r})$.

‡ The position of the maximum of the function $r^2\rho_3(\mathbf{r})$, expressed as a fraction of the bond length.

with those of the same model (model II) of the diamond analysis (paper II). The total-electron redistributions, O, caused by the octupole functions, are very similar [diamond 0·33 (4), silicon 0·33 (2)] and the positions of the maxima of $r^2\rho_3(\mathbf{r})$ as fractions of the bond lengths are not very different [diamond 0·56 (3), silicon 0·500 (6)]. The total-electron redistributions, H, caused by the hexadecapoles differ somewhat [diamond 0·24 (7), silicon 0·08 (1)].* The R factors are: diamond, $R = 0{\cdot}0094$; silicon, $R = 0{\cdot}0028$ (2). The relative effect of bonding on the silicon charge density might be expected to be smaller than that of diamond by a factor between 2·3 (the ratio of the number of electrons in the atoms) and 5 (the ratio of the number of electrons in the cores). The silicon R factor is smaller than that of diamond by the factor 3·4. The silicon GoF [4·3 (4)] is larger than that of diamond (2·9), which is consistent with the smaller errors in the structure factors for the former.

Since Aldred & Hart (1973*a*) had found evidence of expansion of the valence shell it was clear that a monopole deformation function would improve the model. A function was chosen of the form

$$\begin{aligned}\rho_0(\mathbf{r}) = \{&PA'[N_0 + N_0(Z_V - 28)r - N_1(Z_V - 42)r^2] \\ &+ PB'(-N_2r^2 + N_3r^3) \\ &+ PC'(-N_2r^2 + N_4r^4)\}\exp(-Z_Vr),\end{aligned} \qquad (4)$$

where $N_i = Z_V^{i+3}/(i+2)!$ are normalization constants. This function integrates to zero and leaves the cusp condition unaltered. As in paper II the least-squares refinement was ill-conditioned with correlation coefficients between the three populations, PA', PB' and PC', greater than 0·9. Henceforth PA' and PB' were fixed at zero and only PC' and Z_V were included as parameters. Following the normalization convention of paper II, namely that the population parameter of a deformation term should indicate the number of electrons transferred from the negative regions to the positive regions, we quote the monopole population, PC, where

$$\begin{aligned}PC &= PC'\int_R^\infty (N_4r^4 - N_2r^2)\exp(-Z_Vr)r^2\,\mathrm{d}r \\ &= PC'(0{\cdot}328533),\end{aligned}$$

with $R = \sqrt{30}/Z_V$ satisfying $\rho_0(\mathbf{R}) = 0$. Unlike the diamond analysis, however, the exponent Z_V did not refine to a high value and the correlation (about 0·5) between it and the B value was not high. Thus it was possible to determine both in the analysis.

Rather than discuss each set of results as the level of the model was extended we shall only consider in detail results at the '$B\ PC\ Z_V\ O\ Z_O\ H$ [3,4]' and '$B\ PC\ Z_V\ Z_O\ H$ [4,4]' levels [Table 3(*a*) and 3(*b*) respectively]. This coding indicates which parameters are varied in the least squares. They are the B value (B), the amplitude (PC) and width (Z_V) of the monopole function as in (4), and the amplitudes (O and H) and width ($Z_O = Z_V$) of the octupole and hexadecapole functions as in (2) and (3). The numbers in square brackets refer to the orders, n_O and n_H respectively. The parameters of the fifth column of Tables 3(*a*) and (*b*) are means of only the first three data sets. The parameters resulting from data set 4 appear somewhat different from those of data sets 1 to 3. This is probably due to the unusually low experimental e.s.d. of the 880 structure factor of data set 4. The correspondingly high weight given to this structure factor in the refinement causes the least-squares parameters to be modified slightly. The final $(\Delta F/\sigma)^2$ for this reflection contributes some 46% and 40% respectively to the final χ^2 of the [3,4] and [4,4] models.

Of prime importance is the GoF parameter, which is 0·79 (11) and 0·78 (5) for the two models representing a reduction by a factor of five compared with the GoF's in Tables 1 and 2. This indicates that both models describe the data adequately, with it assumed that the experimental e.s.d.'s are accurate. The R factors are near 0·0007, half of the value from Aldred & Hart's (1973*b*) analysis. The particularly low weighted R factor of 0·0002 for data set 3 may be a consequence of the unusually low e.s.d. ($\sigma = 0{\cdot}001$) for the 111 structure factor.

The B values for both models are similar to each other and to that for the $B\ O\ Z_O\ H$ [4,4] refinement of Table 2. These results are 0·008 greater than those of Aldred & Hart (1973*b*) [who obtained $B = 0{\cdot}227$ (3) at 92·2 K and $B = 0{\cdot}461$ (3) at 293·2 K].

On the other hand, there are some differences in the electron-density parameters. The monopole and hexadecapole populations are smaller, while the octupole population is larger in the [4,4] analysis than in the [3,4] analysis. The octupole and hexadecapole populations are considerably larger than those of the $B\ O\ Z_O\ H$ analysis. The sign of the monopole population is such as to redistribute electrons from near the nucleus ($r < R$) to regions further from the nucleus ($r > R$). Since R, as a fraction of the bond length, is 0·54 (2), the overlap of the neighbouring atom results in the function having little direct effect on the charge density along the bond. However, the deformation density in the bond is a sum of the octupole and hexadecapole amplitudes and these increase substantially with the inclusion of the monopole term. The values of the sums (O and $|H|$) for the mean values from Table 3(*a*) and (*b*) are larger than the corresponding sum for the $B\ O\ Z_O\ H$ refinement (Table 2) by 0·41 and 0·26 for the [3,4] and [4,4] analyses respectively. These increases are approximately equal to the monopole populations of 0·27 (4) and 0·34 (4). The inclusion of the monopole term results in a more diffuse octupole and hexadecapole, the maximum of $r^2\rho_3(\mathbf{r})$ increasing to a fraction, 0·61 (1) for the [4,4] analysis, and 0·62 (1) for the [3,4] analysis, of the bond length.

---

* Note that the redistribution into each bond is $O/4$ for the octupole and $H/8$ for the hexadecapole.

The influence of the monopole term is more readily appreciated by inspection of Figs. 1 and 2. Fig. 1 shows the calculated deformation density in a section through the $(1\bar{1}0)$ plane for data set 3 with the [4,4] model of Table 3(*b*). This may be compared with the result (Fig. 2) for the same model with the monopole expansion term omitted ($PC = 0$). The effect of the monopole term is to elongate the bond deformation density across, rather than along, the bond axis. This result makes it clear that an adequate description of the non-spherical components of the electron density depends strongly on the accurate representation of the spherical component.

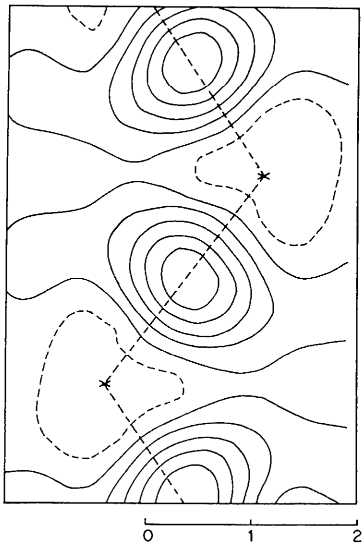

Fig. 1. Deformation density in $(1\bar{1}0)$ plane for data set 3 with the [4,4] model of Table 3(*b*). Contour intervals at 0·027 e Å^{-3}. Negative contours broken.

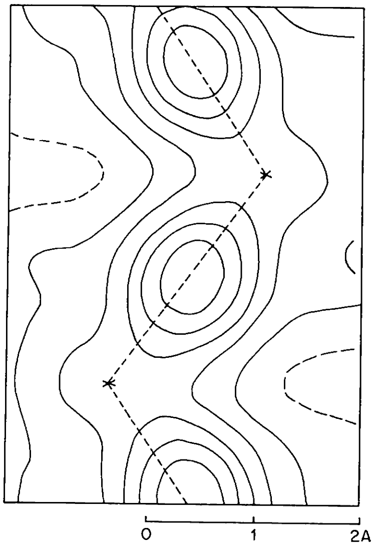

Fig. 2. Deformation density as in Fig. 1, but with $PC = 0{\cdot}0$ (no radial expansion term). Contour intervals at 0·029 e Å^{-3}. Negative contours broken.

The deformation density in Fig. 2 is closely similar to that obtained by Dawson (1967*b*, Fig. 4*b*) for silicon using three independent sets of carefully-measured data available at that time. Comparison with the final result for the accurate, absolute structure factor data for Aldred & Hart (1973*b*) (Fig. 1) gives an indication of the limitations for resolution of charge-density detail inherent in data of standard comparable to that analysed by Dawson (1967*b*).

Anomalous-dispersion corrections

Closer inspection of Table 3(*a*) and (*b*) shows a systematic difference between the results obtained with Mo $K\alpha_1$ radiation and those with Ag $K\alpha_1$ radiation. Until this stage of the analysis the anomalous-dispersion corrections had been fixed at Cromer's (1965) values. When we included the term $\Delta f'$ as an adjustable parameter, the GoF decreased by 0·03, 0·05 and 0·19 for data sets 1, 2 and 4, but increased by 0·04 for data set 3. The systematic differences between data sets were reduced. There was very high correlation between $\Delta f'$ and the B value. The resulting $\Delta f'$ values were 0·081 (8), 0·090 (6) for data sets 1 and 3 (Mo $K\alpha_1$ radiation) and 0·050 (7), 0·044 (7) for sets 2 and 4 (Ag $K\alpha_1$ radiation). The mean values for $\Delta f'_{\rm Mo}$ and $\Delta f'_{\rm Ag}$ are shown in Table 4. This table gives a summary of calculated, inferred and measured values of these anomalous-dispersion corrections. Its dispersion is as great as the list of measured values of the silicon 222 structure factors, shown in Table 6. Our results, which are imprecise because of the high correlation with the B value, lie between the theoretical results of Cromer (1965) and of Cromer & Liberman (1970). They are in poor agreement with the theoretical values of Wagenfeld, Kühn & Guttman (1973), and those determined by Aldred & Hart (1973*b*) from their analysis of this data. While the present work was in progress Cusatis & Hart (1975) made an independent measurement of the dispersion corrections by scanning X-ray interferometry, and their results are in good agreement with ours.

Table 4. *Anomalous-dispersion corrections* ($\Delta f'$)

	Mo $K\alpha$	Ag $K\alpha$
Theoretical		
Cromer (1965)	0·090	0·060
Cromer & Liberman (1970)	0·072	0·042
Wagenfeld *et al.* (1973)	0·101	0·0706
Experimental		
Aldred & Hart (1973*b*)	0·103	0·073
Cusatis & Hart (1975)	0·086 (2)	0·057 (3)
Present work	0·085 (7)	0·047 (7)

Predicting the 222 structure factor

The value of the 'forbidden' 222 reflection in silicon has been the subject of much discussion (Fehlmann & Fujimoto, 1975). Aldred & Hart (1973*a*) did not measure this structure factor but its value can be inferred from the charge-density parameters. In paper II emphasis was placed on the hazards of applying least-squares parameters to calculations of properties which are poorly defined by the data. Not forgetting that such estimates are likely to be strongly model-dependent, we calculated the value of $f_{222}\exp(-M)$ at each level of our model, where f_{222} is the scattering factor due to the antisymmetric component of the electron distribution. The results are shown in Table 5, together with the GoF and R factors, which may be seen to fall as the model becomes more refined. The last five models shown all have a GoF of a little less than unity (except for data set 4) and thus should be adequate descriptions of the data. There is, however, a relatively large variation in the predicted 222 structure amplitudes within these five models. The room-temperature values lie in the range 0·16–0·20. This prediction of our analysis is shown in Table 6, together with Aldred & Hart's (1973*b*) prediction and a collection of directly-measured values from the literature.

Close inspection of Table 5 shows that the room-temperature values of $f_{222}\exp(-M)$ are consistently larger by 0·012 (3) e than the values at 92·2 K. We estimate that the error in the $f_{222}\exp(-M)$ values is such as to make this a significant discrepancy. After division by the Debye–Waller factor the discrepancy, now in the size of the f_{222} values, becomes 0·015 (3). The higher value for the room-temperature f_{222} is a consequence of the slightly larger octupole exponent Z_O, at room temperature. At face value it amounts to a prediction that the antisymmetric distortion of the charge density due to bonding, or at least its 222 Fourier component, increases with temperature.

There have been several studies, both theoretical and experimental, of the temperature dependence of the 222 reflection, all for temperatures near 300 K and above. A discussion of these is presented in the Appendix. The evidence from this existing work for the validity of the convolution approximation as applied to the 222 reflection in silicon is inconclusive. However, the measurements and calculations all indicate that the contribution to F_{222} from the antisymmetric charge distribution decreases with increase in temperature. Our results therefore predict a temperature dependence which is in the opposite direction to these higher-temperature results. The larger exponent, Z_O, at room temperature compared with that at 92·2 K causes the observed temperature dependence of f_{222} in our results and seems to be analogous to the detection of a large-exponent bond-directed dipole term, positively correlated with the amplitude of thermal motion, on the hydrogen atoms in the melamine analysis (paper V). The latter was ascribed to failure of the convolution approximation.

We are unable to make a positive statement about whether our results are really a consequence of failure of the convolution approximation. Our interpretation is complicated by uncertainty about the size of the anharmonic correction to the data of Aldred & Hart (1973*a*). The much larger value of $\beta = 5{\cdot}42\,(54)\ \times$

Table 5. *The model dependence of the GoF and R indices, and of* $f_{222}\exp(-M)$

The model-coding scheme is explained in the text. The values of $f_{222}\exp(-M)$ are in e atom^{-1} and shown as '222'. Values of $10^4\,R$ are shown as 'R'. Those $f_{222}\exp(-M)$ values which were not calculated are designated 'n.c.'.

	Data set 1			Data set 2			Data set 3			Data set 4		
Temperature	92·2 K			92·2 K			293·2 K			293·2 K		
Radiation	Mo $K\alpha_1$			Ag $K\alpha_1$			Mo $K\alpha_1$			Ag $K\alpha_1$		
Model	GoF	R	222	GoF	R	222	GoF	R	222	GoF	R	222
Valence density												
$B\,Z$	6·8	63	n.c.	8·5	67	n.c.	7·5	64	n.c.	6·1	59	n.c.
$\lvert 3,4\rvert\ B\,Z\,O$	5·2	49	n.c.	6·0	50	n.c.	5·7	51	n.c.	5·5	50	n.c.
$\lvert 3,4\rvert\ B\,Z\,O\,H$	4·5	42	n.c.	4·9	44	n.c.	4·9	42	n.c.	4·7	38	n.c.
Deformation density												
B	10·3	72	0·0	13·1	76	0·0	53·3	198	0·0	10·6	72	0·0
$\lvert 4,4\rvert\ B\,O\,Z_O H$	4·7	30	0·170	4·5	30	0·919	4·3	28	0·712	3·8	25	0·164
$B\,PC\,Z$	4·9	36	0·0	5·7	34	0·0	5·2	37	0·0	4·3	35	0·0
$\lvert 4,4\rvert\ B\,PC\,Z\,O$	2·8	17	0·211	2·7	20	0·216	2·2	19	0·207	2·5	15	0·214
$\lvert 3,4\rvert\ B\,PC\,Z\,O\,H$	2·8	20	0·227	2·5	21	0·225	2·3	18	0·222	2·6	18	0·210
$\lvert 4,4\rvert\ B\,PC\,Z\,O\,H$	0·84	8	0·184	0·88	9	0·190	0·69	6	0·186	1·22	10	0·205
$\lvert 3,4\rvert\ B\,PC\,Z\,O\,Z_O\,H$	0·76	6	0·143	0·91	9	0·148	0·69	5	0·156	1·13	8	0·162
$\lvert 4,4\rvert\ B\,PC\,Z\,O\,Z_O\,H$	0·77	6	0·172	0·83	8	0·178	0·73	6	0·189	1·09	8	0·188
$\lvert 4,4\rvert\ B\,PC\,Z\,O\,Z_O\,H\,Z_H$	0·82	6	0·166	0·88	8	0·177	0·79	6	0·182	1·13	8	0·189
$\lvert 4,4\rvert\ B\,PC\,Z\,O\,H\,\Delta f'$	0·81	6	0·176	0·83	8	0·183	0·73	6	0·186	1·03	7	0·195

Table 6. *Silicon room temperature* $|f_{222}\exp(-M)|$ *values*

Direct measurements	Value (e atom^{-1})
Hewat *et al.* (1969)	0·11
De Marco & Weiss (1965)	0·180 (10)
Roberto & Batterman (1970)	0·182 (5)
Jennings (1969)	0·185 (4)
Fujimoto (1974)	0·188 (2)
Colella & Merlini (1966)	0·192
Renninger (1960)	0·194
Fehlmann & Fujimoto (1975)	0·206 (4)
Cramb (1970)	0·22 (2)
Göttlicher & Wölfel (1959)	0·223
Mean	0·188 (31)
Weighted mean*	$0{\cdot}189_6\ (3_5)$
Indirect measurements	
Aldred & Hart (1973*b*)	0·169 (5)
Present (overall)	0·16–0·20
Present [4,4] models†	0·185–0·195
Present [3,4] models†	0·155–0·165

* The weighted (or least-squares) mean of those values quoting an error estimate, given by $\bar{x} = \Sigma\, w_i x_i / \Sigma\, w_i$, $\sigma(\bar{x}) = \mathrm{GoF}(\Sigma\, w_i)^{-1/2}$, with $w_i = [\sigma(x_i)]^{-2}$ (GoF = 2·2).

† The range of values of $f_{222}\exp(-M)$ (at room temperature) of those models with GoF $\simeq$ 1 and with the radial orders given by [4,4] and [3,4]. Note that the former value is in excellent agreement with the weighted mean of the experimental values.

10^{-12} erg Å^{-3} obtained by Roberto *et al.* (1974) at room temperature, compared with the reasonably constant value of $\beta \sim 2{\cdot}7 \times 10^{-12}$ erg A^{-3} at the higher temperatures, suggests that the effective one-particle potential approximation is not good, at least for anharmonic terms, at room temperature and below. This conclusion holds, even if quantum effects are accounted for within the one-particle potential model, since the β-value as determined by Roberto *et al.* (1974) is scarcely affected at 293 K. It is likely, therefore, that the value of β at 92·2 K will be larger than that at room temperature, in line with the experimentally observed increase in β in going from higher temperatures to 300 K. Such an increase in β at 92·2 K would be in the right direction to decrease the differences in f_{222} at the two temperatures. Similarly, if the room-temperature value of β obtained by Roberto *et al.* (1974) were smaller, in close agreement with the high-temperature values, the differences in our f_{222} values would again be reduced. A definite conclusion, therefore, awaits accurate measurements for β for silicon at room temperature and below, presumably by using the high-angle reflections in a neutron-diffraction experiment.

Residuals

The mean GoF's of our final models are about 0·8. This indicates that our model is an adequate description of the data, and that any additional elaboration of the model would (probably) result in an increase in the GoF. The final values of $\mathrm{sgn}(\Delta F)[\Delta F/\sigma(F)]^2$, where sgn is the sign function [$\mathrm{sgn}(x) = x/|x|$], should be randomly distributed about zero with a dispersion measured by the root mean square value of $\mathrm{sgn}(\Delta F)[\Delta F/\sigma(F)]^2$. We estimate the latter to be about 2·0, whereas the observed dispersion is much smaller than this. This examination of residuals leads us to conclude that the e.s.d.'s that we have been using are too large by a factor of about 4. This conclusion is supported by the observation (Hart, 1975) that the errors quoted in Table 3 of Aldred & Hart (1973*a*) are root mean square deviations from the mean, rather than estimates of the standard deviation in the mean. The central-limit theorem of statistics predicts that the uncertainty in the mean is a factor $(n-1)^{1/2}$ smaller than this, where n, the number of reported observations, is here between 10 and 20 for each reflection.

The above discussion has relevance only to random errors in the measurements. An indication of both the systematic and random, *i.e.* total, errors is provided by a comparison of the structure factors at the two wavelengths, at each temperature. This comparison was made by Aldred & Hart (1973*a*), Fig. 5, where it may be verified that the errors assigned by Aldred & Hart (1973*a*) to the structure factors are of the right order to just cover the total errors evident from the plots. It may be concluded, therefore, that weights based on the errors quoted by Aldred & Hart (1973*a*) will be of approximately the right size to account not only for the relatively small random errors, but also for the rather larger systematic errors.

Conclusions

The absolute structure factor data of Aldred & Hart (1973*a*) for silicon form the most accurate set available for any substance. Consequently, it provides a higher resolution of features in the electron distribution than that currently available for diamond and other first-row atom structures. We have used this data to differentiate between various models for the electron density in silicon. In particular, we have shown that a valence-density approach would require a more complicated type of basis set to represent second-row atom charge distributions than the one which has been found adequate with the level of accuracy available for first-row atoms. The deformation-density approach, with the isolated atom used as a reference, proved capable of modelling the electron density with a monopole term, representing an expansion of the valence electrons, and an octupole and a hexadecapole term, each obeying the atomic site symmetry. The monopole term, which has a marked effect on the deformation-density distribution, was not significant in the data analysed by Dawson (1967*b*). This difference in the results obtained from the Aldred & Hart (1973*a*) data compared with those obtained from earlier data indicates that highly accurate structure-factor measurements are required if anything more than the gross features of the charge distribution are to be extracted from crystals with similar bonding effects.

With the deformation-density model, our results are in agreement with the measurements of Cusatis & Hart (1975) for the real dispersion corrections, $\Delta f'$, at Mo $K\alpha$ and Ag $K\alpha$ wavelengths. We were also able to estimate the values of the scattering factor f_{222} for the 222 reflection at 92·2 and 293·2 K. The differing values of f_{222} at the two temperatures could be interpreted as evidence for a breakdown of the convolution approximation. However, the observed temperature dependence of f_{222} is influenced by the anharmonic force constant β, which has been assumed to be the same at both temperatures as the value measured at room temperature by Roberto *et al.* (1974). Failure of the one-particle potential description as a result of quantum effects could lead to different conclusions about the temperature behaviour of the 222 structure factor.

An analysis of the residuals of our final models has revealed that the precision of the experimental structure factors is higher than indicated by the errors quoted by Aldred & Hart (1973*a*), if these are interpreted as the e.s.d.'s for the observations. Nevertheless, the errors assigned by Aldred & Hart (1973*a*) are of the right order to account for the combined systematic and random errors inherent in the measurements.

APPENDIX

In experimental studies of the 222 reflection in silicon neutron-diffraction results have been used to separate out the anharmonic contributions, $F_{\rm anh}$, from the X-ray structure factor, $F_{\text{X-ray}}(222)$, and obtained the part due to the bond, $F_{\rm bond}$, with the relations

$$F_{\text{X-ray}}(222) = F_{\rm bond} - F_{\rm anh}. \qquad (A1)$$

The temperature dependence of $F_{\rm bond}$ may then be described in terms of a Debye–Waller factor, M_b, for the bond with

$$F_{\rm bond} = 8 f_b \exp(-M_b), \qquad (A2)$$

where we initially assume that f_b is independent of temperature.

With this procedure the neutron and X-ray results of Roberto, Batterman & Keating (1974) over a temperature range from 288 to 1093 K indicate that $M_b = 1{\cdot}2\ (1) M_c$, where M_c is the Debye–Waller factor of the core, obtained from the Debye temperature. The 1974 work of Roberto *et al.* supersedes the earlier X-ray work of Roberto & Batterman (1970) and the neutron measurements of Keating, Nunes, Batterman & Hastings (1971), which gave a somewhat lower value for M_b.

The X-ray measurements of Fujimoto (1974), from 300 to 900 K, in combination with the more recent neutron work of Roberto *et al.* (1974), give an M_b of about $1{\cdot}4 M_c$, in substantial agreement with the results of Roberto *et al.* (1974). Additional measurements by Fujimoto (1974) of the pressure dependence of $F_{\text{X-ray}}(222)$ up to 5·2 kbar might tend to suggest that f_b in (A2) has negligible implicit temperature dependence. However, the relation between the pressure and temperature-dependent effects on $F(222)$ is not clear-cut, especially as silicon is somewhat anomalous in that it contracts on melting.

Fujimoto (1974) has also made theoretical calculations on the mean-square vibrational amplitude of the bonding charge, assuming it to be located at the midpoint of neighbouring atoms. Using the experimental phonon-dispersion curves of Dolling (1963) he obtained $M_b = 0{\cdot}74\ (5) M_c$ (*cf.* $M_b = 1{\cdot}0 M_c$ for completely correlated motion of nearest neighbour atoms and $M_b = 0{\cdot}5 M_c$ for completely uncorrelated motion). Chelikowsky & Cohen (1974) have calculated the silicon charge density using an energy-dependent non-local pseudopotential. Yang & Coppens (1975) have obtained valence density maps from experimental data for silicon, principally those of Aldred & Hart (1973*a*). These maps are in substantial agreement, both in bond shape and bond height, with the theoretical valence densities obtained by Chelikowsky & Cohen (1974). Chelikowsky & Cohen also calculated the implicit temperature variation of f_b from an assumed temperature-dependent form for the crystalline potential and obtained a decrease in f_b with increasing temperature. They further assumed that f_b was multiplied by a Debye–Waller factor, $M_b = 0{\cdot}5 M_c$, corresponding to uncorrelated motion of near-neighbour atoms. With this model they were able to obtain agreement with the results of Roberto *et al.* (1974) over the entire temperature range.

If the antisymmetric component of the charge density were vibrating rigidly with the nucleus, then M_b in (A2) would equal M_c and the remaining temperature dependence would be taken up by f_b. The results reviewed above are, however, inconclusive with respect to validity or failure of the convolution approximation for silicon, as the implicit temperature dependence of f_b has not been established with absolute certainty.

References

Aldred, P. J. E. & Hart, M. (1973*a*). *Proc. R. Soc. London, Ser. A*, **332**, 223–238.

Aldred, P. J. E. & Hart, M. (1973*b*). *Proc. R. Soc. London, Ser. A*, **332**, 239–254.

Allen-Williams, A. J., Delaney W. T., Furina, R., Maslen, E. N., O'Connor, B. H., Varghese, J. N. & Yung, F. H. (1975). *Acta Cryst.* A**31**, 101–115.

Berkovitch-Yellin, Z. & Leiserowitz, L. (1975). *Acta Cryst.* A**31**, S224.

Chelikowsky, J. R. & Cohen, M. L. (1974). *Phys. Rev. Lett.* **33**, 1339–1342.

Clementi, E. (1965). *IBM J. Res. Dev.* **9**, Suppl. *Tables of Atomic Functions.*

Colella, R. & Merlini, A. (1966). *Phys. Status Solidi*, **18**, 157–166.

Cramb, J. A. (1970). Fourth Year Report, School of Physics, Univ. of Melbourne, Australia.

Cromer, D. T. (1965). *Acta Cryst.* **18**, 17–23.

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

Cusatis, C. & Hart, M. (1975). *Anomalous Scattering*, edited by S. Ramaseshan & S. C. Abrahams, pp. 57–68. Copenhagen: Munksgaard.

Dawson, B. (1967*a*). *Proc. R. Soc. London, Ser. A*, **298**, 255–263.

Dawson, B. (1967*b*). *Proc. R. Soc. London, Ser. A*, **298**, 379–394.

Dawson, B. (1975). *Advances in Structure Research by Diffraction Methods*, Vol. 6, edited by R. Mason & W. Hoppe. Braunschweig: Vieweg.

Dawson, B., Hurley, A. C. & Maslen, V. W. (1967). *Proc. R. Soc. London, Ser. A*, **298**, 289–306.

Dawson, B. & Willis, B. T. M. (1967). *Proc. R. Soc. London, Ser. A*, **298**, 307–315.

De Marco, J. J. & Weiss, R. J. (1965). *Phys. Rev. A*, **137**, 1869–1871.

Dolling, G. (1963). *Inelastic Scattering of Neutrons in Solids and Liquids*, p. 37. Vienna: IAEA.

Doyle, P. A. & Turner, P. S. (1968). *Acta Cryst.* A**24**, 390–397.

Fehlmann, M. & Fujimoto, I. (1975). *J. Phys. Soc. Jpn*, **38**, 208–215.

Fujimoto, I. (1974). *Phys. Rev. B*, **9**, 591–599.

Göttlicher, S. & Wölfel, E. (1959). *Z. Electrochem.* **63**, 891–901.

Harel, M., Hecht, M. & Hirshfeld, F. L. (1975). *Acta Cryst.* A**31**, S224.

Harel, M. & Hirshfeld, F. L. (1975). *Acta Cryst.* B**31**, 162–172.

Hart, M. (1975). Private communication.

Hehre, W. J., Ditchfield, R., Stewart, R. F. & Pople, J. A. (1970). *J. Chem. Phys.* **52**, 2769–2773.

Hewat, A. W., Prager, P., Stephenson, J. D. & Wagenfeld, H. (1969). *Acta Cryst.* A**25**, S213.

Hirshfeld, F. L. (1971). *Acta Cryst.* B**27**, 769–781.

Hohenberg, P. & Kohn, W. (1964). *Phys. Rev.* **136**, B864–B871.

International Tables for X-ray Crystallography (1962). Birmingham: Kynoch Press.

Jennings, L. D. (1969). *J. Appl. Phys.* **40**, 5038–5064.

Keating, D., Nunes, A., Batterman, B. & Hastings, J. (1971). *Phys. Rev. B*, **4**, 2472–2478.

Kurki-Suonio, K. & Ruuskanen, (1971). *Ann. Acad. Sci. Fenn. Ser. A*6, p. 358.

McConnell, J. F. & Sanger, P. L. (1970). *Acta Cryst.* A**26**, 83–93.

Mair, S. L. & Wilkins, S. W. (1976). *J. Phys. C*, **9**, 1145–1158.

Price, P. F. & Maslen, E. N. (1978). *Acta Cryst.* A**34**, 173–183.

Price, P. F., Maslen, E. N. & Delaney, W. T. (1978). *Acta Cryst.* A**34**, 194–203.

Price, P. F., Varghese, J. N. & Maslen, E. N. (1978). *Acta Cryst.* A**34**, 203–216.

Renninger, M. (1960). *Z. Kristallogr.* **113**, 99–103.

Roberto, J. B. & Batterman, B. W. (1970). *Phys. Rev. B*, **2**, 3220–3226.

Roberto, J. B., Batterman, B. W. & Keating, D. (1974). *Phys. Rev. B*, **9**, 2590–2599.

Srebrenik, S. & Bader, R. F. W. (1975). *J. Chem. Phys.* **63**, 3945–3961.

Stewart, R. F. (1972). *Electron Population Analysis with Generalized X-ray Scattering Factors.* Unpublished.

Stewart, R. F. (1973*a*). *J. Chem. Phys.* **58**, 1668–1676.

Stewart, R. F. (1973*b*). *J. Chem. Phys.* **58**, 4330–4438.

Sygusch, J. (1974). *Crystallographic Studies of two Antibiotics and of Diglycolic Acid Experimental Charge Density Analysis of Diglycolic Anhydride.* Thesis, Univ. Montreal.

Wagenfeld, H., Kühn, J. & Guttman, A. J. (1973). *Abstr. 1st Eur. Crystallogr. Conf.*, Bordeaux.

Yang, Y. W. & Coppens, P. (1975). *Solid State Commun.* **15**, 1555–1559.