Redetermination of Absolute Structure Factors for Silicon at Room and Liquid Nitrogen Temperatures*

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Abstract

Many new determinations of silicon structure factors have been made in the last few years providing confidence in dynamical diffraction methods and challenging the basis of available theories. The first analysis of experiments done in the early 1970s (Aldred and Hart 1973) has been repeatedly compared with theories and more recent experiments. A number of minor problems have come to light, for example, the crucial need to detect strain gradients and small changes in the accepted values of some parameters. Fortunately, the raw data was published by Aldred and we have reanalysed these experiments, making corrections for strain gradients. These new results still comprise the only low temperature high precision data on silicon, which is an important feature since it is becoming increasingly clear that anharmonic effects are insufficiently well measured in silicon compared with other features of the electron density.

1. Introduction

With the publication of a complete set of structure factors for silicon based on measurements of Pendellösung fringes in the integrated Laue-case reflection from perfect crystals [Saka and Kato (SK) 1986], we now have high precision datasets by three independent methods. The first dataset [Aldred and Hart (AH) 1973] was interpreted and tested for internal consistency within several crystallographic models by Price, Maslen and Mair (PMM) in 1978. The second dataset, which determined structure factors from the oscillations in double crystal rocking curves [Teworte and Bonse (TB) 1984] agreed with those published earlier, so no further analysis was necessary at the time.

Partial datasets relating to the 222, 442, 622 and very high orders such as 777, 888, 999 and 880, 10 10 0, 12 12 0 focussed sharply on questions relating to bonding, anharmonicity, core wavefunctions and anomalous dispersion. Those topics are outside the scope of this paper, which seeks to analyse the internal consistency of the three major datasets and to establish an acceptable consolidated dataset for further theoretical analysis. It is unfortunate that all of the attempts to intepret these high precision silicon data during the last ten years or so have apparently been published just as significant new experiments were published.

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Table 1. Comparison between the SK Fourier transform

f_{SK} of the Clementi wavefunctions and the DW

transform f_{DW} of the same wavefunctions

hkl	f_{SK}	f_{DW}	$f_{SK} - f_{DW}$ (me)
111	10.5286	10.5454	-16.8
220	8.7102	8.7082	2.0
311	8.1644	8.1618	2.6
400	7.5077	7.5069	0.8
331	7.1833	7..1831	0.2
422	6.7022	6.7030	-0.8
333	6.4392	6.4404	-1.2
511	6.4392	6.4404	-1.2
440	6.0350	6.0364	-1.4
531	5.8106	5.8116	-1.2
620	5.4637	5.4647	-1.0
533	5.2706	5.2714	-0.8
444	4.9718	4.9723	-0.5
551	4.8054	4.8058	-0.4
711	4.8054	4.8058	-0.4
642	4.5480	4.5482	-0.2
553	4.4045	4.4045	0
731	4.4045	4.4045	0
800	4.1822	–	–
733	4.0581	..	–
660	3.8658	3.8655	0.3
822	3.8658	3.8655	0.3
555	3.7583	3.7580	0.3
751	3.7583	3.7580	0.3
840	3.5913	–	–
753	3.4979	–	–
911	3.4979	–	–
664	3.3524	–	–
844	3.1438	–	–
880	2.5333	–	–

Our interest in this problem was rekindled by some curious inconsistencies in the SK paper comparisons with AH and TB data. To take some extreme examples we noted that, on the theory side, the famous Clementi–Hartree–Fock wavefunctions have been subjected to a new Fourier transform program. As Table 1 shows, eight of the first eleven structure factors differ from those of Dawson and Willis (DW) (1967) by more than one millielectron (me) unit and the crucial 111 differs by 0·16%, an intolerable situation when most experimental work is necessarily aiming for better than 0·1% precision so as to elucidate features in bonding and anharmonicity.

Both Fourier transforms use the same Clementi (1965) wavefunctions.   N. Kato (personal communication, 1987) has pointed out typographical errors in some theoretical structure factors (Table 4 in SK) which have been corrected in our Table 1. We were also surprised by the result of the SK analysis which showed (SK Table 5) agreement to within about 0·2% between the AH, TB and SK data for all high order data. To take an extreme example, the 844 Bragg reflection room temperature f values are 2·198 (Ag Kα_1) (TB), 2·227 (Mo Kα_1) (TB), 2·19 (Ag Kα_1) (AH), 2·211 (Mo Kα_1) (AH) and 2·1798 (0·4 Å) (SK). After correction for the wavelength dependent anomalous dispersion these span a range of 1·4%, yet the agreement in

SK Table 5 appears to be within $0 \cdot 5\%$. The reason for this contradiction seems to be a fortuitous choice of theoretical dispersion corrections (Cromer and Liberman 1970) and a fitted temperature factor based only on the SK data.

We believe that it will be productive in this paper, if we analyse the internal consistency of the AH, TB and SK silicon data with the absolute minimum of theoretical intervention. As a first step we have recalculated structure factors from the raw data by Aldred (1971) and Aldred and Hart (1973). We then calculate, for each dataset, the electronic scattering amplitude per atom:

$$f_0 = f_{obs} - f' \exp(-M) - 0 \cdot 0038 \exp(-M), \tag{1}$$

where the last term represents the nuclear scattering amplitude. The total correction amounts to less than $0 \cdot 1e$ units and is the minimum necessary for the experimental data to be compared.

2. Reanalysis of the AH Data

Aldred (1971) and Aldred and Hart (1973) made about 2000 measurements of Pendellösung fringe position and crystal thickness. Although measurements were made over a range of crystal thicknesses to detect the presence of strain, they did not analyse the data in terms of the established theory of dynamical diffraction in weakly distorted crystals. We have now reanalysed the data within that framework.

The effect of a uniform strain gradient, represented by the parameter p (Penning and Polder 1960; Kato 1964; Hart 1966), is to increase the interference order n_0 in a Pendellösung fringe pattern to n, where

$$n = \tfrac{1}{2} n_0 \{(1+p^2)^{\frac{1}{2}} + p^{-1} \operatorname{arcsinh} p \}. \tag{2}$$

For small deformations, such as those present in dislocation free silicon crystals, we may approximate this as

$$\frac{n}{t} = \frac{n_0}{t} \left(1 + \frac{\beta^2 t^2}{24} \right). \tag{3}$$

Here $p = \tfrac{1}{2}\beta t$ and, in the simple case of a uniform temperature gradient G, $\beta = 2\alpha_T \tan\theta \, G/\chi_h$, where t is the crystal thickness, θ is the Bragg angle, α_T the linear thermal expansion coefficient and $\chi_h = -e^2\lambda^2 F_h/\pi mc^2 V$, and where these symbols have their usual meanings.

In all of the AH data there was marginally significant evidence of strain, but we nevertheless fitted, using conventional least-squares, the observed fringe spacings n/t to equation (3). In more than 75% of the datasets the slope of the curve was positive (as it must be!) and in no case was the new strain free Pendellösung distance t/n_0 different from the AH value t/n by more than one standard deviation. Typical datasets are shown in Fig. 1.

Using the established value for the harmonic Debye–Waller temperature factor (Price *et al.* 1978) of $B = 0 \cdot 4676(14)$ Å^2 the room temperature results were corrected to $T = 293 \cdot 2$ K. The complete data are listed in Table 2.
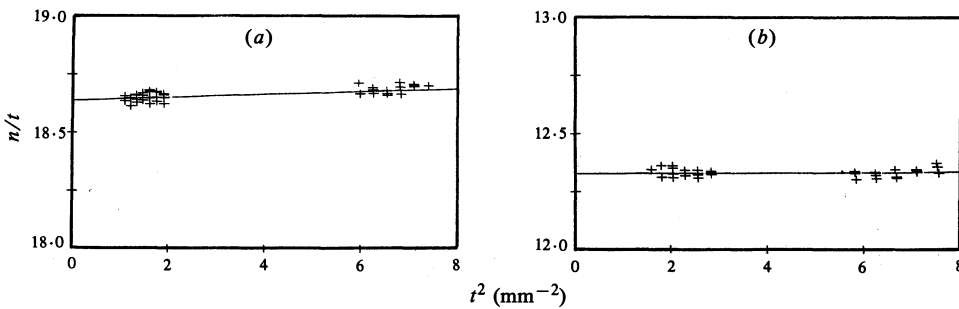
Fig. 1. Typical AH datasets showing fringe order, crystal thickness and the least-squares fit to the dynamical diffraction equation (3) for crystals containing a strain gradient: (a) Ag Kα_1 (400) at 92 K and (b) Ag Kα_1 (331) at 293 K.

Table 2. AH silicon data reanalysed giving the total

scattering amplitude per atom

Standard deviations are given in parentheses; one redundant
digit is given to avoid truncation and rounding errors in later analysis

hkl	T = 92·2 K		T = 293·2 K	
	Mo Kα_1	Ag Kα_1	Mo Kα_1	Ag Kα_1
111	10.7720(145)	10.6710(230)	10.6881(88)	10.6674(36)
220	8.5898(51)	8.5785(48)	8.4783(34)	8.4405(53)
311	7.9408(49)	7.9066(22)	7.7650(26)	7.7391(34)
400	7.3023(61)	7.2756(22)	7.0803(19)	7.0557(17)
331	7.0698(32)	7.0832(35)	6.8107(29)	6.7837(38)
422	6.4831(43)	6.4377(41)	6.2090(33)	6.1598(40)
333	6.1984(44)	6.1527(46)	5.8696(39)	5.8313(34)
511	6.1959(59)	6.1627(45)	5.8673(47)	5.8403(47)
440	5.7708(91)	5.7287(72)	5.4115(28)	5.3820(37)
444	4.6258(44)	4.5927(37)	4.1943(37)	4.1790(23)
642	4.1895(90)	4.1430(89)	3.7247(87)	3.7117(68)
660		3.4124(58)	2.9833(32)	2.9558(38)
555	3.3339(116)	3.3087(69)	2.8705(65)	2.8407(26)
844	2.6492(84)	2.6524(51)	2.1997(45)	2.1766(47)
880		2.0206(88)	1.5774(121)	1.5732(30)

3. Reduction to Zero Wavelength

The correction of data to account for the nuclear scattering is straightforward and we subtract $0·0038\exp(-M)$ from each measured value. Anomalous dispersion is more difficult since no absolute measurements exist for the energies used in the SK experiments. There is abundant evidence that theoretical values of f' in the short wavelength limit are not satisfactory (Creagh 1985; Smith 1987). We must therefore use experimentally determined values obtained by X-ray interferometry (Cusatis and Hart 1975) for Ag Kα_1 and Mo Kα_1 wavelengths. We can also use the difference measurements of Saka and Kato (1987) in a least-squares adjustment involving two fixed values, the slope $df''/d\lambda$ from those experiments and an assumed power law

dependence for f'. Deutsch and Hart (1988) found the following values:

	0·400 Å	0·415 Å	0·5594 Å	0·7093 Å
f'	0·0285(20)	0·0305(20)	0·0568(26)	0·0863(18).

The correction for anomalous dispersion amounts to $f' \exp(-M)$ and, since this is a small effect, we can take any of the published Debye–Waller factors, for example the SK value $\exp(-M) = \exp\{-3\cdot877\times10^{-3}(h^2 + k^2 + l^2)\}$.

Table 3. Residuals f per atom (value−mean) in me units

hkl	TB Ag (PE)	TB Mo (PE)	SK 0·4 Å (PE)	AH Ag (SD)	AH Mo (SD)	f_{mean}
111	−4.3(5)	7.5(6)	−4.6(0.1)	5.0(3.6)	−3.4(8.8)	10.6025
220	−6.8(5)	11.6(10)	−1.5(0.9)	−6.3(3.3)	2.9(3.4)	8.3881
311	−1.4(5)	3.4(6)	1.1(0.1)	−0.4(3.4)	−2.6(2.6)	7.6814
400	0.3(4)	−6.4(4)	3.1(0.1)	3.0(1.7)	−0.1(1.9)	6.9958
331	4.4(4)	−7.0(4)	0.7(0.1)	1.1(3.8)	0.7(2.9)	6.7264
422	−9.4(4)	5.8(4)	−3.5(0.1)	−7.6(4.0)	14.8(3.4)	6.1123
333	0.0(5)	1.5(3)	−5.6(0.1)	−3.7(3.4)	8.0(3.9)	5.7806
511	−1.0(5)	6.5(4)	3.5(0.1)	−4.7(4.7)	−4.2(4.7)	5.7906
440	3.2(4)	1.2(4)	−0.3(0.7)	−3.8(3.7)	−0.3(2.8)	5.3324
444	−4.0(3)	6.6(6)	−3.7(0.3)	5.0(2.3)	−4.1(3.7)	4.1239
551	−1.6(4)	−0.8(3)	2.3(0.1)	–	–	3.9349
642	–	–	−4.1(1.4)	7.3(6.8)	−3.2(8.7)	3.6558
800	−7.8(4)	3.2(3)	4.7(1.0)	–	–	3.2485
660	0.2(2)	6.0(2)	−3.4(0.6)	−4.1(3.8)	1.2(3.2)	2.9143
555	2.1(4)	2.2(4)	−1.9*(2.7)	−5.2(2.6)	2.6(6.5)	2.8009
844	6.0(3)	14.8(4)	7.0(1.5)	−15.4(4.7)	−12.5(4.5)	2.1506
880	6.0(4)	–	−0.8(1.8)	4.2(3.0)	−9.4(12.1)	1.5325
Mean	−0.88	3.74	−0.41	−1.71	−0.64	
SD	4.7	5.8	3.6	6.1	6.6	

*Wavelength is 0·415 Å.

Table 3 summarises the available data including all hkl for which three separate techniques have been employed. In Table 3 we have calculated equation (1) for each of the five datasets, showing the deviation from the mean of (usually) five values together with the authors own estimates of probable error (PE) or standard deviations (SD). It is immediately apparent from the scatter of residuals that all five datasets are of similar quality with typical errors of about 3–5 me for all hkl. Three datasets have mean residuals near zero and the other two have mean residuals ranging from −2 to 4 me. Overall the situation is very satisfactory, but in percentage terms not what has been claimed in the past. In the worst case (844) there is a total spread of 1·4% in structure amplitude per atom, but in other very important reflections the total spread is only 0·11% (111), 0·059% (311) and 0·12% (400).

4. Low Temperature Datasets

Since all of the low temperature AH measurements were made at the same temperature only anomalous dispersion corrections are necessary for the 92·2 K data
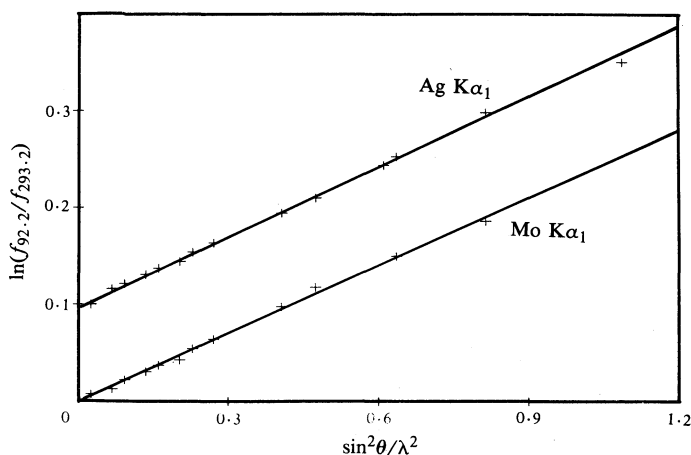
Fig. 2. Direct comparison between room and liquid nitrogen temperature measurements. The Ag $K\alpha_1$ data have been shifted vertically by 0·1 for clarity. Note that the two gradients are identical and that no pair of *hkl* measurements deviates significantly from the line.

in Table 2. We used the same f' as before with the temperature factor refined by Price *et al.* (1978) [$B = 0 \cdot 2357(26)$ Å^2]. If the crystal structure is the same at 92·2 K and at 293·2 K then the ratio of structure amplitudes per atom should be equal to the ratio of the harmonic temperature factors. In detail, $\ln(f_{92.2}/f_{293.2})$ should be linear in $\sin^2\theta/\lambda^2$. As Fig. 2 shows, this is the case and we conclude that the structure of the covalent silicon bond is the same at both temperatures.

Overall the agreement between the five room temperature datasets and the two low temperature datasets is very satisfactory. We can therefore have confidence in the three independent Pendellösung methods, the demonstrated quality of the silicon crystals used and the anomalous dispersion corrections. Nevertheless, in detailed analyses by AH, PMM and many other authors, including most recently by Spackman (1986), it has long been clear that there are significant discrepancies between some experimental data and theoretical models. Until now, both the anomalous dispersion corrections and the anharmonicity were in doubt.

5. Comparison with Pseudopotential Models

We can also analyse the resulting mean structure amplitudes per atom given in Table 3 against theoretical models. Most authors computing scattering amplitudes by *ab initio* pseudopotential methods have published values only for low order Bragg reflections and then with an implied precision of about 10 me. Table 4 compares measured with theoretical scattering amplitudes for the free atom model [Dawson's (1967) Fourier transform of the Clementi (1965) wavefunctions, see Table 1], for four early pseudopotential calculations (Stukel and Euwema 1970) and the most recent pseudopotential calculations of Yin and Cohen (1982).

None of the reflections listed is significantly affected by anharmonic thermal scattering. To correct the theoretical data for the harmonic Debye–Waller factor we

Table 4. Comparisons between various theoretical models and the mean experimental scattering amplitudes given in Table 3

Residuals are given in me. SL, KSG, SL-RHF and KSG-RHF are from Stukel and Euwema (1970); D-C from Dawson (1967) and Clementi (1965); and YC from Yin and Cohen (1982)

hkl	f_{mean}	SL	Δf_{SL}	KSG	Δf_{KSG}	SL-RHF	Δf_{SL-RHF}
111	10.6025	10.88	-133.2	10.69	35.5	10.86	-130.4
220	8.3881	8.77	-73.9	8.64	10.2	8.72	-61.1
311	7.6814	8.11	-38.1	8.01	3.3	8.03	-5.6
400	6.9958	7.54	-21.0	7.44	-0.2	7.46	-5.2
331	6.7264	7.34	-12.2	7.21	26.3	7.27	-16.4
422	6.1123	6.81	0.6	6.68	23.3	6.71	13.6
333	5.7086	6.51	18.7	6.38	33.1	6.40	34.9
511	5.7906	6.55	-10.0	6.42	4.2	6.44	6.1
440	5.3324	6.17	-10.2	6.02	10.8	6.05	5.0
444	4.1239	5.12	0	4.96	0	4.99	0
Mean Δf_{Th}			-31.0		16.3		-17.7
SD			46.3		13.5		49.6

hkl	KSG-RHF	$\Delta f_{KSG-RHF}$	D-C	Δf_{D-C}	YC	Δf_{YC}
111	10.70	36.3	10.5454	181.8	10.699	11.8
220	8.67	3.3	8.7082	-54.4	8.615	2.5
311	8.05	-7.2	8.1618	-143.9	7.976	-4.5
400	7.49	-10.4	7.5069	-60.9	7.380	3.6
331	7.26	22.3	7.1831	-60.3	7.149	22.7
422	6.73	27.2	6.7030	8.6	6.610	17.5
333	6.41	61.1	6.4404	-18.3	6.307	24.2
511	6.45	32.2	6.4404	-7.2	6.336	6.9
440	6.07	25.4	6.0364	4.3	5.940	0
444	5.04	0	4.9723	0	–	–
Mean Δf_{Th}		21.1		-16.7		10.6
SD		22.7		88.0		10.3

have simply assumed, for the highest order Bragg reflection listed, that $\exp(-M) = f_{mean}/f_{theory}$ and this value has been scaled by $\sin^2\theta/\lambda^2$ and applied to the remainder of the measurements. We adopt this very simple approach, rather than a least-squares fit between model and room temperature data, to avoid mixing between theoretical and experimental artifacts in the goodness of fit indicators. The columns headed Δf list the differences between the theoretical and experimental scattering factors, and $\Delta f_{Th} = f_{mean} \exp(+M) - f_{Th}$.

Bearing in mind that estimated errors are typically 4 me for the experimental data and at least 10 me for the bonded atom theoretical data, a number of useful conclusions can be drawn from the experimental (Table 3) and theoretical (Table 4) tables of residuals. First, is the obvious conclusion that the free atom theory shows

worse agreement with experiment than any of the pseudopotential results. But the mean difference Δf_{D-C} is only $-16 \cdot 7$ me, a scaling error (if it is that) of $-0 \cdot 2\%$ overall. Since, over all models, this difference ranges from $-31 \cdot 0$ to $21 \cdot 1$ me, whereas the experimental mean residuals range from only $-1 \cdot 71$ to $3 \cdot 74$ me, it is likely that this is a theoretical rather than an experimental problem.

These values also show that only the 111, 220, 311, 400, 331 and 333 are strongly altered in the bound crystal. Note, however, that the fact that the 333 does change, whereas the 511 hardly changes, is an important feature of the bonding problem to which theories must relate. When Aldred and Hart (1973) analysed their data against the same four Stukel and Euwema (1970) models they obtained almost identical results: $\Delta f_{SL} = -108 \pm 21$ me, $\Delta f_{KSG} = 26 \pm 15$ me, $\Delta f_{SL-RHF} = -27 \pm 46$ me and $\Delta f_{KSG-RHF} = -16 \pm 30$ me. Thus, the addition of three new datasets and correction of the AH data for residual strain gradients has not qualitatively changed the conclusions of any past comparisons between theories and experiments. However, the agreement between independent experiments now gives added confidence on which theories can be strongly interrogated.

Considerable theoretical progress has been made. We can now conclude that the Yin and Cohen (1982) results are precisely in agreement with experiment since the agreement with experiment is $\Delta f_{YC} = 9 \cdot 7 \pm 10 \cdot 0$ me. It may be useful finally to pinpoint and describe the remaining problems which relate mainly to forbidden reflections and anharmonicity.

6. Yin–Cohen Scattering Factors and Experimental Values

The 331, 422 and 333 reflections (Table 4) differ by around 20 me from experiment, whereas the experimental data have standard deviations of 4 me (331), 10 me (422) and 5 me (333). There is a significant deviation in this $\sin\theta/\lambda$ range between experiment and the YC model. The 333/511 pair of reflections differ by -10 ± 7 me according to experiment (Table 3). The corresponding theoretical value is -30 ± 14 me. On the basis of the strong reflections we can therefore conclude that the estimated error in the theoretical structure factors is about 10 me, while the appropriate internal experimental standard deviation is about 5 me, independent of the order, hkl, of Bragg reflection. Since, on the basis of both theory and experiment, the silicon bond structure amplitudes per atom are less than 10 me (Tischler and Batterman 1984) for both the 442 and 622 Bragg reflections, there may be no basis for any theoretical discussion of those two reflections at present.

The only other bond specific Bragg reflection which has been measured in silicon is the 222. The position has been reviewed recently by Alkire *et al.* (1982). While Yin and Cohen found $f_{222} = 190$ me, models based on AH data (Price *et al.* 1978), which will be similar to model values deduced by the same technique from Table 3, give $f_{222} = 162$ to 204 me. By contrast, the direct γ-ray measurement gives $f_{222} = 191 \pm 1$ me per atom which is in excellent agreement with present conclusions (Alkire *et al.* 1982).

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