PHYSICAL REVIEW B VOLUME 40, NUMBER 17 15 DECEMBER 1989-I

Thermal motion of atoms in crystalline silicon: Beyond the Debye theory

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(Received 28 August 1989)

Evidence is presented for nonrigid thermal vibrations of crystal-bound silicon atoms, using an extensive set of measured structure factors F_m accurate to 0.1%. A model allowing for a different Debye-Waller factor (DWF) for each electronic shell is found to fit all F_m well with four such factors. DWF's refined from F_m using calculated shell-by-shell partial structure factors yield good agreement with earlier results derived from low-order reflections but not with *ab initio* shell-model calculations. Also, no evidence is found for an anharmonic term in the atomic potential.

The thermally induced vibrations of a crystal-bound atom are conventionally treated as those of a rigid body and accounted for in x-ray diffraction by the inclusion of the Debye-Waller (DW) factor $\exp(-Bq^2)$ in the structure amplitude[1] $F(h,k,l)$, where B is the Debye parameter, $q=\sin\theta/\lambda$, and λ and θ are the radiation wavelength and the Bragg angle, respectively. It was realized early[2] that in a more realistic model the different shells of the electronic charge distribution associated with the atom should move differently, and thus dynamically distort the atom. In practice, however, the rigid-atom or "convolution" approximation proved to be an extremely good one and experimental evidence for deviations from it are at best inconclusive and indirect. In particular, for monoatomic molecules, a *single* DW factor was found to be sufficient to account for the influence of thermal motion on *all* $F(h,k,l)$ of a given crystal at a fixed temperature. Thus, dynamical deformation theories employing shell,[3] adiabatic-bond-charge,[3,4] and valence-force-potential[5] models concentrated on calculating a value for a single effective Debye parameter B_{eff} and its temperature dependence for a limited number of model crystals. On the experimental side, temperature-dependent high-accuracy intensity measurements for "forbidden" reflections in silicon and germanium[6-8] indicated a possible difference in the Debye parameters of the bonding charges B_b and that of the rest of the atom ("core"), B_C. Quantitative estimates of the difference range, however, from[8] $B_b=0.5B_c$ to[6,7] $B_b=1.4B_c$.

In this paper, we present for the first time direct evidence for a nonuniform thermal vibration of the crystal-bound silicon atom, based on a high-accuracy ($<0.1\%$) set of *Pendellosung*-measured structure amplitudes of silicon extending to high orders. A model allowing a different vibrational amplitude, and hence a different B, for each electronic shell of the Si atom is shown to account well for the measured $F(h,k,l)$. Least-squares-fitted values for the B's are given, and the results are compared with theoretical predictions.[3]

The higher-order $F(h,k,l)$ employed here were determined from measured thin-crystal Laue-case rocking curves at various energies as detailed in Ref. 9. The recent revision[10] of the Aldred and Hart[11] low-order F values, on which Ref. 9 relied for calibration, entailed a corresponding revision of the high-order F's. The revised values are given in Table I, which also lists anomalous-dispersion-correction values[12] $\Delta f'$ and nuclear scattering and anomalous-dispersion-corrected[9] F values F_1. Our recent study[13] of microstrain levels in Si ensures freedom from strain effects in the listed $F(h,k,l)$, with a possible exception of $F(10,10,0)$ as discussed in Ref. 9.

The full data set used in the refinement is given in Table II. F_1 is the average of the values in the last column of Table I for each (h,k,l). F_2, taken from Ref. 10, are essentially the revised Aldred and Hart[11] data, but include as well all the relevant high-precision $F(h,k,l)$ measured by Teworte and Bonse[14] and Saka and Kato.[15] The theoretical subshell-by-subshell partial structure factors were calculated by directly Fourier transforming the Hartree-Fock free-atom wave functions of Clementi.[16] the distortions of the free-atom charge distribution induced by crystal bonding were extensively studied by *ab initio* calculations[17] as well as Fourier summation and multipole-expansion refinements where terms up to hexadecapole were included.[18-21] These studies show that bonding effects in F decrease with increasing q and become negligible for $q \gtrsim 0.8$ Å^{-1} with present-day measurement accuracy. This conclusion is also supported by Cummings and Hart's[10] recent comparison of several theoretical calculations with experiment. Following their practice, a phenomenological bonding correction is calculated as the difference between the measured and calculated free-atom structure amplitudes: $\Delta f_b = F_2\exp(Bq^2) - \sum_i f_i$, where f_i ($i=1s,2s,\ldots$) are taken from Table II

TABLE I. High-order structure factors F_{meas} for silicon, measured using the *Pendellosung* method of Ref. 9. Measurements at different energies for the same (h,k,l) are indicated by (a), (b), ... $\Delta f'$ are the corresponding anomalous-dispersion-correction terms from Ref. 12 and F_1 are the structure factors corrected for nuclear scattering and anomalous dispersion.

$h\,k\,l$	E (keV)	F_{meas}	$\Delta f'$	F_1
4 4 4 (a)	13.956	4.2533(93)	0.1382	4.1359
(b)	17.687	4.2043(85)	0.0819	4.1335
6 6 0	16.587	2.9939(97)	0.0942	2.9202
8 8 0 (a)	23.262	1.5700(21)	0.0488	1.5383
(b)	29.492	1.5565(43)	0.0319	1.5350
7 7 7 (a)	17.445	1.3277(42)	0.0868	1.2780
(b)	22.109	1.3074(23)	0.0568	1.2736
(c)	24.426	1.3083(34)	0.0463	1.2803
8 8 8 (a)	17.445	0.9039(30)	0.0863	0.8645
(b)	22.109	0.8911(20)	0.0568	0.8646
(c)	27.912	0.9039(44)	0.0358	0.8866
10 10 0	17.445	0.8268(10)	0.0863	0.7887
9 9 9	22.109	0.6123(32)	0.0568	0.5910
12 12 0	22.109	0.4563(11)	0.0568	0.4388

and $B = 0.4632$ Å^2 as obtained from several[9,11,19] F refinements for $0 \le q \le 1$ Å^{-1} data.

The Δf_b values obtained are listed in Table II. Taking into account the average $\sigma = \pm 4 \times 10^{-3} e$ accuracy[10] of the measured F's we note that indeed $\Delta f_b < 2\sigma$ in Table II for all entries beyond $(h,k,l) = (4,4,0)$, as expected.

Following now the conventional practice of a single atomic-scattering amplitude f (the sum of the partial ones and Δf_b in Table II) and a single Debye parameter,[9,11,19] $B = 0.4632$ Å^2, to calculate $F_c = f \exp(-Bq^2)$, systematic deviations as large as 12% from the measured $F(h,k,l)$ occur for high q values, as can be seen in Fig. 1. As discussed above, bonding effects are limited to low-order reflections, and thus cannot account for deviation

TABLE II. Consolidated $F(h,k,l)$ data set. F_1 are the average values for each (h,k,l) taken from the last column of Table I. F_2 are the measured low-order $F(h,k,l)$ of Ref. 10 and Δf_b are the static bonding charge distortions calculated as detailed in the text. The partial subshell-by-subshell structure amplitudes $f_{1s}, \ldots, f_{3p}$ were calculated by direct Fourier transform of the wave functions of Ref. 16.

$h\,k\,l$	F_1	F_2	Δf_b	f_{1s}	f_{2s}	f_{2p}	f_{3s}	f_{3p}
1 1 1		10.6025	0.1833	1.9937	1.8639	5.6128	0.6871	0.3874
2 2 0		8.3881	−0.0520	1.9834	1.6588	5.0367	0.0576	−0.0287
3 1 1		7.6814	−0.1409	1.9772	1.5475	4.7274	−0.0379	0.0529
4 0 0		6.9958	−0.0569	1.9670	1.3792	4.2641	−0.0674	−0.0366
3 3 1		6.7264	0.0648	1.9609	1.2876	4.0138	−0.0582	−0.0216
4 2 2		6.1123	0.0139	1.9509	1.1488	3.6365	−0.0330	−0.0007
3 3 3		5.7806	−0.0126	1.9448	1.0730	3.4315	−0.0181	0.0085
5 1 1		5.7906	−0.0009	1.9448	1.0730	3.4315	−0.0181	0.0085
4 4 0		5.3324	0.0106	1.9349	0.9578	3.1210	0.0028	0.0192
4 4 4	4.1347	4.1239	0.0075	1.9036	0.6660	2.3357	0.0359	0.0304
5 5 1		3.9349	0.0023	1.8978	0.6219	2.2167	0.0381	0.0306
6 4 2		3.6558	0.0073	1.8882	0.5546	2.0343	0.0402	0.0302
8 0 0		3.2485	−0.0049	1.8730	0.4608	1.7784	0.0404	0.0287
6 6 0	2.9202	2.9143	0.0016	1.8581	0.3818	1.5600	0.0384	0.0266
5 5 5		2.8009	0.0027	1.8525	0.3554	1.4863	0.0373	0.0258
8 4 4		2.1506	0	1.8142	0.2106	1.0701	0.0280	0.0201
8 8 0	1.5367	1.5325	0	1.7582	0.0816	0.6648	0.0153	0.0132
7 7 7	1.2789		0	1.7262	0.0371	0.5051	0.0099	0.0103
8 8 8	0.8719		0	1.6538	−0.0166	0.2638	0.0023	0.0056
10 10 0	0.7887		0	1.6415	−0.0213	0.2345	0.0014	0.0051
9 9 9	0.5910		0	1.5774	−0.0328	0.1194	−0.0012	0.0028
12 12 0	0.4388		0	1.5143	−0.0308	0.0494	−0.0021	0.0014

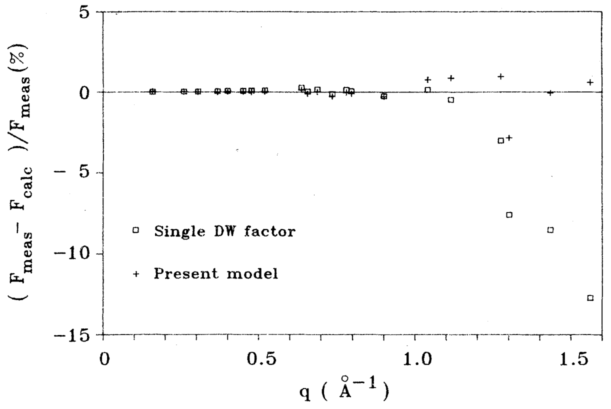

FIG. 1. Relative difference between the measured $F(h,k,l)$ of Table II for conventional single-Debye-parameter representation (□) and for the present one (+), Eqs. (1) and (2). The breakdown of conventional Debye theory at high q is clearly seen. Note the improvement upon allowing different thermal motion for different electronic shells.

from free-atom F values at $1 \leq q \leq 1.6$ Å^{-1}. Furthermore, the q dependence of the deviations, increasing with q, is the *opposite* of that expected for bonding distortions, or radial expansion of the valence-shell orbitals. Finally, Yin and Cohen's[17(b)] *ab initio* calculations clearly show that the core electrons are extremely inert to changes in the valence shell. A change in the valence configuration from s^2p^2 to sp^3 resulted in a change of $0.8 \times 10^{-3} e$/atom at most in the core structure factors. We conclude, therefore, that bonding distortions are a highly unlikely cause for the observed deviation. Clearly the approximation of a single DW factor over the full range of the data[9,20] has to be relaxed, although it provides satisfactory agreement with the measured $F(h,k,l)$ for $q < 1$ Å^{-1}.

To account for these deviations, a model allowing for a different DW for each electronic shell was assumed:

$$F_c = \sum_i f_i \exp(-B_i q^2) , \tag{1}$$

where $f_i = f_{1s}, f_{2s}, \ldots, f_{3p}, \Delta f_b$, $q = (h^2+k^2+l^2)^{1/2}/(2a_0)$, and $a_0 = 5.431\,02$ Å is the lattice constant of Si. A series of nonlinear least-squares fits of Eq. (1) to F_1 and F_2 were carried out, starting with $B_1 = B_{1s}$ and B_2 common to the rest of the atom, then $B_1 = B_{1s}$, $B_2 = B_{2s}$, and B_3 common to the rest of the atom and so on. A number of other combinations were also tried. The results indicated that even the high-quality data of Table II will not support the refinement of more than three or four B values. The best fit is obtained for a four-parameter fit, which yields

$$\begin{aligned} B_{1s} &= 0.531 \pm 0.003 \text{ Å}^2 , \\ B_{2s} &= 0.941 \pm 0.045 \text{ Å}^2 , \\ B_{2p} &= 0.283 \pm 0.012 \text{ Å}^2 , \\ B_{3s,3p,\Delta f_b} &= 0.58 \pm 0.15 \text{ Å}^2 . \end{aligned} \tag{2}$$

A three-parameter fit leaves B_{1s} unchanged, B_{2s} decreased by 10%, and $B_{2p,3s,3p,\Delta f_b}$ increased by 10% relative to the present B_{2p}. Using a larger number of different B's leaves the present values unchanged and no decrease is obtained in the residual sum of squares (RSS). Attempts to minimize the effect of bonding by excluding from the fit an increasing number (≤ 10) of the lowest-order F_2 values invariably yielded B_i values equal, within the cited errors, to those of Eq. (2). Furthermore, the use of different B_i for each shell n, rather than subshell nl, results in an increased RSS. Thus a four-parameter fit with $B_i = B_{1s}, B_{2s,2p}, B_{3s,3p}, B_{\Delta f_b}$, while decreasing the somewhat high B_{2s} of Eq. (2), yields RSS of 2.3×10^{-3}, much higher than the RSS of 0.93×10^{-3} obtained for the values in Eq. (2).

As can be seen in Fig. 1, the present model fits the data well over the full q range. The deviation of $F(10,10,0)$ at $q = 1.3$ Å^{-1} is due to strain as discussed in Ref. 9. The results of the alternative fits discussed above as well as the consistent trend observed in the subshell-by-subshell fits as the number of B's is increased lend additional confidence in the values listed in Eq. (2).

An alternative approach[3] to that presented above is the adoption of a *single* effective Debye parameter, which is q dependent rather than constant, i.e., $F = f \exp[-B_{\text{eff}}(q)q^2]$. Values of $B_{\text{eff}}(q)$ calculated from the measured F_1 and F_2 and from F_c of Eqs. (1) and (2) are plotted in Fig. 2. As can be seen, excellent agreement is obtained. For $Q < 1$ Å^{-1}, $B_{\text{eff}}(q)$ is fairly constant and agrees well with the best conventional constant-B refinements, $B_0 = (0.4613 \pm 0.027)$,[11] (0.4632 ± 0.0041),[9] and (0.4632 ± 0.0011) Å^2,[19] and slightly less well with $B_0 = (0.4676 \pm 0.0014)$ Å^2 of Ref. 21. The *ab initio* shell-model calculations of Reid and Pirie[3] for shells having 1 and 2.87 electrons, also given in Fig. 2, considerably overestimate the measured values although it is possible that an extension of these calculations beyond $q = 1$ Å^{-1} will yield a better agreement there.

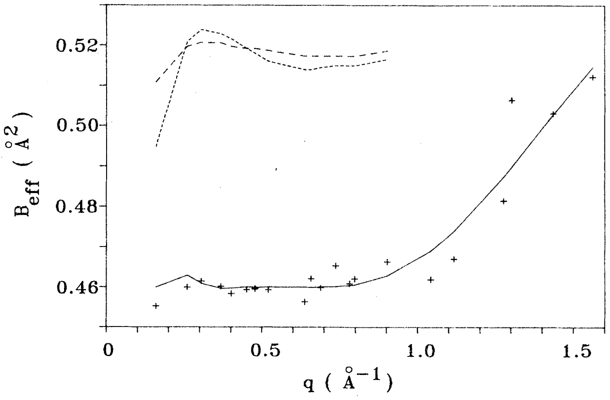

FIG. 2. Effective Debye-parameter, B_{eff}, variation with q. Note the good agreement between experiment (+) and the present representation (——) which allows for different thermal motion of different electronic shells. The *ab initio* shell-model calculations of Ref. 3 for a shell of 1 (— — —) and 2.87 (· · ·) electrons clearly overestimate the measured values.

We would also like to point out that the inclusion of an anharmonic term in the effective one-particle potential experienced by the atom results[11] in an extra temperature factor in F. As this factor is proportional to βhkl, where β is the anharmonic force constant, it is expected to influence $F(7,7,7)$ and $F(9,9,9)$ most. However, no deviation from the trend set by neighboring F's is observed for these structure factors. The accuracy of the data of Table I therefore places an upper limit of $\beta < 1.2$ eV Å^{-3} on the anharmonic force constant. This result is in good agreement with the conclusions of Aldred and Hart,[11] $\beta < 1.8$ eV Å^{-3}, and the forbidden 442 and 622 reflection x-ray[22] and neutron[23] measurements of Batterman and co-workers, who find $\beta \approx 1.4$ eV Å^{-3}, but it is in contrast to the neutron forbidden 222 reflection results of Roberto *et al.*[6] and Nunes,[24] who find a much higher $\beta = 3.38$ eV Å^{-3}. Further high-accuracy measurements of F's for high q values are required to settle this question.

In conclusion, clear evidence for deviations from the rigid-atom model was presented. The deviations were accounted for by assigning a different Debye parameter B to each electronic shell of the atom. Four B values were found to provide a good description of the highest-accuracy structure-factor data set available for silicon over its complete q range. However, no theoretical basis for the observed Debye-parameter variation with electronic shell, and in particular the large B_{2s}, can be given at this stage. The extension of the body of measured $F(h,k,l)$ to higher q values is clearly indicated.

The support of the Science and Engineering Research Council (U.K.) and the Carlsberg Foundation, Denmark, are gratefully acknowledged.

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