Lattice dynamical Debye-Waller factor for silicon

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The mean-square amplitude of vibration of silicon at 293 K has been determined by a lattice-dynamical procedure. A Born–von Kármán model has been used to fit phonon dispersion data from inelastic neutron-scattering measurements. The force-constant model included the first six nearest neighbors in the diamond-type lattice. The least-squares results from the fitting of the force constants were used to carry out variance analyses of properties dependent on the harmonic model. The density of phonon states was determined by sampling an even mesh of 5.7 billion points in the unique part of the Brillouin zone. Moments of the frequency distribution up to eighth order are tabulated. The frequency distribution function was used to calculate a $\langle u^2_{\mathrm{LD}} \rangle$ for silicon. The result is $0.005\,941 \pm 0.000\,021\ \text{Å}^2$. An Einstein-type potential of Dawson and Willis was used to extract an anharmonic force constant from the temperature dependence of neutron-diffraction measurements of silicon carried out by Batterman and co-workers. These measurements were restricted to the weak reflections from the (222), (442), and (622) diffracting planes. With the use of the lattice-dynamical value for the vibrational amplitude of silicon the result for the β_{DW} anharmonic constant is $18.58 \pm 0.27\ \mathrm{N\,m^{-1}\,Å^{-1}}$.
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I. INTRODUCTION

For the last several decades very accurate measurements of crystalline silicon structure factors by the method of x-ray Pendellösung fringes have appeared in the crystal physics literature.[1–4] In addition, rather weak reflections from this crystal with space group $Fd\bar{3}m$ have been measured as integrated Bragg diffraction intensities at essentially kinematic conditions. The associated diffracting planes are (222),[5] (442), and (622).[6,7] The nonzero intensities can only occur due to nonspherically symmetrical scattering factors of odd order spherical surface harmonics at the silicon atom sites that have point-group symmetry $\bar{4}3m$. These measured structure factors of silicon have served as a benchmark for experimental determination of electron-density distributions and physical properties that depend on the charge-density distribution in the crystal. Very recently an extensive data set from diffraction with W $K\alpha_1$ radiation at approximate kinematic conditions was reported and used for a construction of a *mean thermal* electron-density distribution.[8] Although the relative cross-section data lack the accuracy of the Pendellösung data, the extension to a $\sin\theta/\lambda$ value of 2.5 Å^{-1} provided the investigators with an unusually high-resolution electron-density map.

The details of the charge-density analysis of accurate structure factors for silicon vary from one investigator to another. Spackman[9] derived a static electron-density distribution with the rigid pseudoatom approximation and sought comparison with solid-state calculations. On the other hand, Deutsch[10] characterized the structure factors with an electron-density distribution that deforms with vibrational motion by the silicon *nucleus*. Sakata and Sato[11] used Pendellösung data to construct the mean thermal electron density by the maximum entropy method. Similarly, the Japanese workers, Yamamoto *et al.*[8] reported a mean thermal valence electron-density map also based on the principle of maximum entropy. Our own interests have focused on the total *mean thermal* charge-density distribution which includes the nuclear charge density as well. In particular we seek a silicon Debye-Waller factor that is not based on an x-ray measurement.

A single-crystal neutron-diffraction experiment generally gives reliable Debye-Waller factors if the diffracting conditions are nearly kinematic. Single crystals of silicon, however, are virtually perfect so that the dynamical scattering of neutrons renders the diffraction experiment intractable for an accurate determination of the mean-square amplitude of vibration $\langle u^2 \rangle$ by the silicon nucleus. A powder-diffraction experiment of silicon with neutrons can and does provide a reasonable determination of the Debye-Waller factor. Baisheng *et al.* report a value of $0.45 \pm .02\ \text{Å}^2$ at 284 K for B which corresponds to a mean-square amplitude of vibration of $0.0059\ \text{Å}^2$ at 293 K.[12] The neutron velocity of 3.34 km/s in the incident beam was far below the minimum velocity of sound in the crystal. Thus the results were not contaminated with thermal diffuse scattering. The precision of the B value was about 4%; a precision of 1% or better is our goal.

Another route to a Debye-Waller factor in a cubic crystal is by a lattice-dynamical sum over all the normal modes of vibration in the crystal. For monatomic cubic crystals the evaluation involves an integration over the vibrational frequency distribution. The appropriate expression was given originally by Blackman.[13] With the use of dispersion curves of the normal modes of vibration, measured by inelastic neutron-scattering techniques, as well as measured Raman spectra and elastic constants, frequency distribution functions can be determined. The actual evaluation requires a

force-constant model of some sort that is used to fit the dispersion curves and other lattice-dynamical data. Reid has given a brief summary of B values for silicon based on several lattice-dynamical models.[14] At 293 K the values vary from 0.516 Å^2 (shell model of Dolling[15]) to 0.473 Å^2 (bond charge model of Dolling and Cowley[16]). Several valence force potential models yielded B values of 0.448, 0.467, and 0.469 Å^2, respectively. The Born-von Kármán model of Zdetsis and Wang[17] led to a value of 0.470 Å^2. The spread of values corresponds to a 14% deviation from a mean of 0.482 Å^2, if the shell result is not treated as an outlier. It would seem that a lattice-dynamical determination of the silicon Debye-Waller factor cannot be used to obtain a value that is precise to 1%. To cite John S. Reid and John D. Pirie in their 1980 publication: ''Indeed, there can be few quantities so apparently straightforward to determine as the Debye-Waller factor but in practise so elusive.''

In the last 20 years, however, it has become easy to undertake the computation of fitting the dispersion curves with Born-von Kármán (BvK) force constants (BvK model), construction of the dynamical matrix elements and solution of the secular equation, sampling the Brillouin zone at a large number of phonon frequencies and modes, and the final calculation of the phonon frequency distribution function. The BvK model is phenomenological and usually requires at least fifth-nearest neighbors for a satisfactory fit to the dispersion data from a diamond-type lattice.[18] This is not a deterrent at the present since in the 1990s more extensive data sets of inelastic neutron scattering by silicon have become available. One can expect a least-squares treatment to be well overdetermined in the ratio of observations to disposable force constants. In addition, a variance analysis of the final results is an easy undertaking. We report below results for a calculated density of phonon states in silicon based on the BvK model. From this distribution function a value for the Debye-Waller factor is determined at 293 K.

A single-particle potential for atomic motion in a diamond-type structure was proposed by Dawson and Willis some years ago.[19] The functional form of this effective Einstein potential is

$$V(\mathbf{r}) = V_0 + \frac{1}{2}\alpha_{\mathrm{DW}}(x^2+y^2+z^2) + \beta_{\mathrm{DW}}xyz, \qquad (1)$$

where V_0, the potential energy of the equilibrium configuration, is taken as zero and the x,y,z refer to displacements from the equilibrium positions. The harmonic force constant is α_{DW} which is related to the mean-square amplitude of vibration as

$$\alpha_{\mathrm{DW}} = \frac{k_B T}{\langle u^2 \rangle}. \qquad (2)$$

The Dawson-Willis potential predicts a T^2 temperature dependence for a class of $|F_{hkl}|$'s which was observed from neutron diffraction by the (222) reflecting planes in silicon.[20] In addition, the T^2 dependence was also observed for neutron reflections from the (442) and (622) planes.[21] If α_{DW} is known, then it's possible to determine β_{DW} from the measured temperature dependence of the integrated intensities from the family of diffracting planes for which $h+k+l = 4n+2$. We report the anharmonic force constant, β_{DW}, based on the data reported by Hastings and Batterman,[21] Roberto, Batterman, and Keating,[22] and the Debye-Waller factor from the present work.

II. BvK MODEL FITS TO DISPERSION DATA AND ELASTIC CONSTANTS

The dispersion data from inelastic neutron-scattering measurements are for the symmetry directions $\Delta[100]$, $\Sigma[110]$, and $\Lambda[111]$ in the Brillouin zone. The secular determinant of the dynamical matrix can be solved in closed form for these directions. The explicit relations between frequencies and BvK force constants out to sixth-nearest neighbor have been given by Herman[18] and Zdetsis.[23] The expressions for the 21 force constants have been confirmed with our own computer code for generating the force-constant matrices in a diamond-type lattice. The only discrepancy occurred for $\delta'_{-}{}'''$ given by Zdetsis. We get the negative of his expression as does Herman, which is $\delta'_{-}{}''' = \frac{1}{2}(\delta'''' - \gamma'''')$. The elastic constants C_{11}, C_{12}, and C_{44} are related to 19 of the 21 BvK force constants according to the method of long waves; the relations are in Zdetsis' paper.[23] The elastic constants do not depend on the antisymmetric off-diagonal elements δ and $\delta'_{-}{}'''$.

A least-squares program was written to fit the BvK force constants to the squares of the measured cyclic frequencies ω^2, for the Δ, Σ, and Λ symmetry directions. First and second derivatives of the dispersion relations given by Zdetsis with respect to the force constants were evaluated explicitly. The elastic constants and an optically measured Raman frequency were included as observational constraints. The gradient and the Hessian of the mean-square surface, a sum of weighted residuals spanned by 21 variables, were determined at any point on the surface.

$$\varepsilon = \sum_{n=1}^{No} w_n (O_n - F(\mathbf{q};\mathbf{P}))^2, \qquad (3)$$

where No is the number of observations, O_n is the mass weighted square of a phonon frequency based on neutron-scattering measurements, $\omega_n^2(\mathbf{q})$ the square of a measured Raman frequency ω_{RA}^2, or elastic constants, which can be related to force constants by the method of long waves.[18,23,24] The w_n is the inverse square of the error cited in the experimental data list. F is an explicit algebraic expression given by Zdetsis which is a function of $\mathbf{q}$, a vector in the Brillouin zone and of $\mathbf{P}$, a vector consisting of the BvK force constants. Let $\Delta_n = [O_n - F(\mathbf{q};\mathbf{P})]$. Then the gradient of ε has the components

$$\partial\varepsilon/\partial P_j = -2\sum_{n=1}^{No} w_n \Delta_n \partial F/\partial P_j, \quad j = 1,...,21 \qquad (4)$$

The Hessian of the mean-square error has the matrix elements

$$\partial^2\varepsilon/\partial P_j\partial P_k$$

$$=2\sum_{n=1}^{No} w_n[(\partial F/\partial P_j)(\partial F/\partial P_k)-\Delta_n\partial^2 F/\partial P_j\partial P_k],$$

$$j=1,...,21, \quad k=1,...,21. \quad (5)$$

Equation (3) was solved for a minimum by a *stabilized* Newton-Raphson method.[25] Several initial values for **P** were submitted to our least-squares program. The starting values included: the 21 BvK force constants given by Zdetsis and Wang,[17] a set equal to 10^{2-n} where n is the ordinal number for nearest neighbor, and 10 for α and β with zero for the remaining 19 force constants. For the cases given here the same stationary point on the ε surface was found. The eigenvalues of the Hessian (5) at this point were all positive, which ensures that a minimum was found.

The experimental neutron data used for the construction of ε are those of Dolling,[15] Nilsson and Nelin,[26] Strauch, Mayer, and Dorner,[27] and Kulda *et al.*[28] Altogether this set of neutron dispersion data is comprised of 189 observations. Some of the measurements are overlapping but the weights differ with larger values (smaller errors) assigned to more recent data. The Raman scattering line of 15.595 $\pm$.015 THz, measured by Parker, Feldman, and Ashkin, has a reported precision better than one part per thousand[29] and was used as an observational constraint for ω_{RA} along with the less precise values reported by Dolling (15.53 $\pm$.23 THz) and Kulda *et al.* (15.69$\pm$.07 THz). The elastic constants were based on the ultrasonic measurements of McSkimin,[30] but no errors were reported. A small summary of results for different silicon single crystals given in Ref. 30 indicates a precision of about 0.5% for the velocity measurements. Accordingly, we have assumed a relative error of 1% in the elastic constants as a basis for statistical weights. The total number of observations No in Eq. (3) is 193 so that the ratio of observations to variables No/Nv is 9.2.

An appropriate assignment of weights proved to be a vexing problem. With weights based on the literature values,[15,26–28] a minimum in Eq. (3) had a χ^2 value [Eq. (8)] of 21.4. On the other hand, when the neutron data were restricted to the 75 frequencies of Dolling, Nilsson, and Nelin used by Zdetsis and Wang[17] the value for χ^2 was 1.52. Both results include the three elastic constants and the optical Raman frequency measurement. Evidently the sixth-nearest-neighbor BvK model of 21 force constants is deficient and/or the data given by Kulda *et al.* have underestimated error bars. A fit to the 73 neutron data in Ref. 28 plus the elastic constants and the optically measured Raman frequency has a χ^2 of 33.5. Yet the quality of fit is rather good in terms of the relative weighted error,

$$R_w=\left(\sum_{n=1}^{No} w_n\Delta_n^2 \Big/ \sum_{n=1}^{No} w_n O_n^2\right)^{1/2}, \quad (6)$$

of 1.61%. The errors cited by Kulda *et al.* lack precision for use as weights in least squares. For example, if an error listed as $\pm$.01 THz is actually $\pm$.014 THz the corresponding difference in weight is nearly a factor of 2. We found in an *ad hoc* fashion that imposing lower limits to the relative error for *all* neutron frequency measurements in a range from 0.001–0.01 in steps of 0.001 resulted in a convergence of all BvK force constants to a constant value well within the associated estimated standard deviations when $\sigma(\nu)/\nu$ was 0.005 or larger. The correlation coefficients between the force constants were dramatically less for $\sigma(\nu)/\nu \geqslant 0.005$ than for the result with weights based on the face values of the cited errors. A result with constant weights for all observations has a χ^2 value of 22.2 and a large number (87 in all) of correlation coefficients (9) among the force constant variables in the ranges $-1.00 \leqslant C_{jk} \leqslant -0.707$ and $0.707 \leqslant C_{jk} \leqslant 1.00$.

TABLE I. Least-squares-fitted values of the force constants for Si (N/m).

1°	α	46.50±0.70
	β	41.01±0.48
2°	μ	2.89±0.29
	ν	5.07±0.33
	λ	−6.74±0.48
	δ	2.10±0.32
3°	μ'	1.54±0.32
	ν'	−1.78±0.30
	λ'	−3.44±0.42
	δ'	−1.64±0.18
4°	μ''	−1.60±0.42
	λ''	2.88±0.61
5°	μ'''	1.59±0.22
	ν'''	0.92±0.29
	λ'''	6.52±0.48
	δ'''	2.39±0.20
6°	μ''''	0.43±0.14
	ν''''	0.54±0.15
	λ''''	−0.43±0.18
	δ''''	−0.20±0.14
	γ''''	0.27±0.12

The BvK force constants by minimization of Eq. (3) with weights based on the reported errors, but *increased if necessary* to a relative precision not less than 0.005, are given in Table I with the estimated standard deviation $\sigma(P_j)$ based on the inverse matrix elements of Eq. (5) and χ^2:

$$\sigma(P_j)=(\chi^2\varepsilon^{jj})^{1/2}, \quad (7)$$

where ε^{jj} is the jjth inverse matrix element of the least-squares Hessian and

$$\chi^2=\varepsilon/(No-Nv). \quad (8)$$

The correlation coefficients C_{jk}, defined below, were rather small:

$$C_{jk}=\varepsilon^{jk}/\sqrt{\varepsilon^{jj}\varepsilon^{kk}} \quad (9)$$

with only three outside the bounds of $\pm 1/\sqrt{2}$. These values were -0.92 for the correlation between δ'''' and γ'''', -0.85 for the $\mu\,\mu'''$ couple and -0.78 for the $\lambda''\,\lambda''''$ pair. Despite the small off-diagonal elements in the inverse Hessian, one should not neglect these terms in computing a variance for some property that depends on the BvK force constants (*vide infra*). The final BvK force constant fits, given in

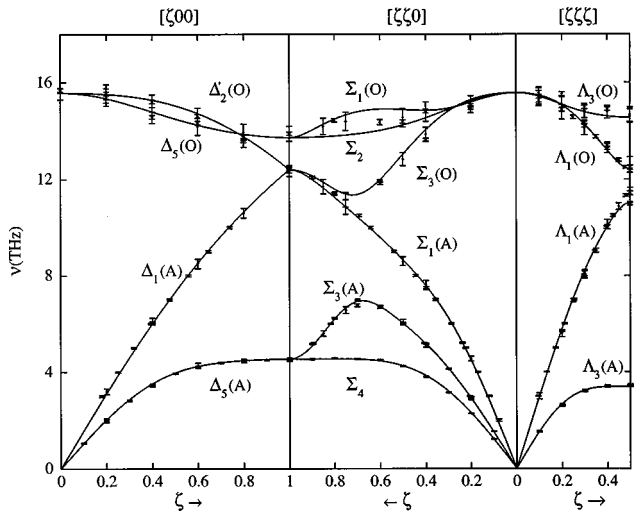

FIG. 1. Dispersion fits for Si.

Table I, had an R_w [cf. Eq. (6)] of 2.54% and a χ^2 value [cf. Eq. (8)] of 5.45. The BvK force constant fits to the dispersion curves in the $[\zeta\ 0\ 0]$, $[\zeta\ \zeta\ 0]$, and $[\zeta\ \zeta\ \zeta]$ directions of the Brillouin zone are shown in Fig. 1.

III. THE PHONON FREQUENCY DISTRIBUTION AND ITS MOMENTS FOR SILICON

The force constants in Table I were used to construct the dynamical matrix $\mathbf{D}(\mathbf{q})$ for a diamond lattice which consists of a 3×3 Hermitian matrix $\mathbf{H}(\mathbf{q})$, and a 3×3 symmetrical matrix $\mathbf{S}(\mathbf{q})$. $\mathbf{S}(\mathbf{q})$ couples the sublattice κ with the sublattice κ' and $\mathbf{H}(\mathbf{q})$ contains coupling among atoms in the same sublattice. A unitary transformation introduced by Lax[31] transforms $\mathbf{D}(\mathbf{q})$ into a 6×6 symmetric matrix $\mathbf{D}'(\mathbf{q})$ with real elements. The 21 matrix elements in $\mathbf{D}'(\mathbf{q})$ can be derived from four prototypes of $\mathbf{D}(\mathbf{q})$.[23] The phonon frequencies for any $\mathbf{q}$ can be determined by solving the 6×6 secular equation

$$|\mathbf{D}'(\mathbf{q})-\mathbf{I}m\omega^2|=0, \tag{10}$$

where $\mathbf{I}$ is the 6×6 identity matrix and m is the mass of the silicon atom.

The unique part of the Brillouin zone was sampled on a uniform mesh of $2^{32.42}$ (or $10^{9.76}$) $\mathbf{q}$ sites, where at each point, the six eigenfrequencies were determined by solving Eq. (10). For the construction of the density of phonon states, 4096 intervals from 0–16 THz were used to make a histogram of frequencies determined at each $\mathbf{q}$ point. The resolution in ν, by this procedure, was 0.0039 THz. The calculated frequency distribution is shown in Fig. 2. The curve displayed here is very similar to Fig. 3 in the paper by Zdetsis and Wang.[17]

The moments for $g(\nu)$ have been calculated up to M_8 where

$$M_n=\frac{\int_0^\infty \nu^n g(\nu)d\nu}{\int_0^\infty g(\nu)d\nu} \tag{11}$$

and are conveniently reported in condensed form with the equivalent Debye cutoff frequency, as recommended by Barron *et al.*:[32]

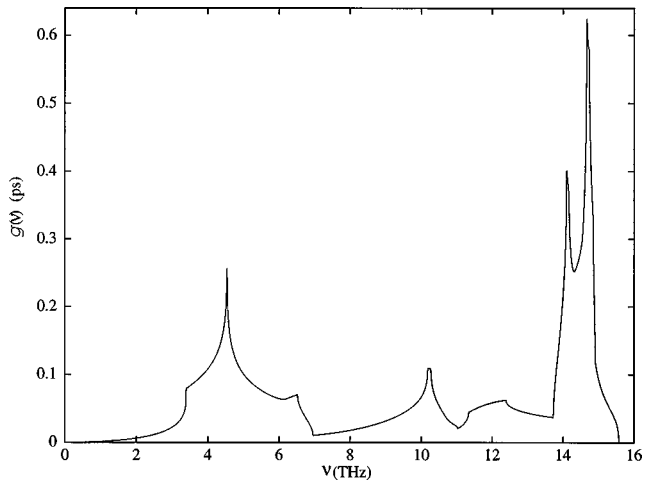

FIG. 2. Density of phonon states for Si.

$$\nu_D(n)=\left[\frac{1}{3}(n+3)M_n\right]^{1/n}, \tag{12}$$

$$\nu_D(0)=\exp\left(\frac{1}{3}+\frac{\int_0^\infty(\ln\nu)g(\nu)d\nu}{\int_0^\infty g(\nu)d\nu}\right), \tag{13}$$

$$\nu_D(-3)=\frac{k_B}{h}\Theta_D(0). \tag{14}$$

$\Theta_D(0)$ in Eq. (14) is the Debye temperature at zero degrees Kelvin. The ν_D are listed in THz as a function of n in Table II. The estimated standard deviations of these ν_D are also listed; these $\sigma(\nu_D)$ values were derived from the inverse matrix elements of the Hessian (5) and the numerical derivatives of the M_n with respect to the 21 force constants. The entries in column B are derived from thermodynamic data and are taken from Ref. 16.

IV. SILICON DEBYE-WALLER FACTOR AND ITS VARIANCE

The density of phonon states, given in the previous section for silicon, can be used to construct thermodynamic

TABLE II. Equivalent Debye frequencies ν_D for Si (THz).

n	A[a]	B[b]
−3	13.398±0.033	13.44
−2	10.974±0.021	11.07
−1	11.434±0.018	11.50
0	12.454±0.021	12.46
1	13.451±0.028	13.37
2	14.181±0.035	14.0
3	14.651±0.039	—
4	14.943±0.042	14.8
5	15.124±0.044	—
6	15.239±0.045	15.0
7	15.313±0.046	—
8	15.362±0.047	—

[a]Based on $g(\nu)$.
[b]Based on thermodynamic data.

properties such as the specific heat. We use our present results to calculate a Debye-Waller factor for silicon at 293 K. The explicit relation, first given by Blackman,[13] is

$$B=\frac{2h^2}{mk_BT}\int_0^\infty g(\nu)\frac{1}{x}\left(\frac{1}{2}+\frac{1}{(e^x-1)}\right)d\nu, \tag{15}$$

where $x=h\nu/k_BT$. The first term in the parentheses of Eq. (15) is due to the zero-point motion and the second includes the temperature dependence. With numerical integration over the density of phonon states, $g(\nu)$ displayed in Fig. 2, our result for B is 0.4691 ± 0.0016 Å^2 or, equivalently, the mean-square amplitude of vibration $\langle u^2\rangle$, is $0.005\,941\pm.000\,021$ Å^2. The average of the lattice-dynamical values for B, reported in Ref. 14, is 0.465 Å^2, if the shell model value of 0.518 Å^2 is rejected as an outlier.

If the Debye temperature Θ_D is less than four or five times T, then it is also possible to use the moments of $g(\nu)$ to calculate a reliable value of B. One has the expansions

$$B(0)=\frac{h}{m}M_{-1}, \tag{16}$$

$$B(T)=\frac{2k_BT}{m}\sum_{n=0}\frac{B_n}{n!}\left(\frac{h}{k_BT}\right)^n M_{n-2}. \tag{17}$$

The B_n in Eq. (17) are the Bernoulli numbers, which are zero for n odd and $\geqslant 3$. The zero-point contribution to B is given in Eq. (16) while Eq. (17) has the temperature-dependent terms. In contrast to diamond, where $B(0)$ is 86% of the Debye-Waller factor at 298 K,[33] $B(0)$ is 0.1864 Å^2, which is 40% of the silicon Debye-Waller factor at 293 K. From the entries in Table II and with

$$M_n=3\nu_D^n/(n+3)$$

the result for the sum in Eq. (17) is 0.2827 Å^2 for $B(T)$ and $B(0)$ from Eq. (16) is 0.1864 Å^2. The sum from Eq. (17) had reached four-decimal-place accuracy by the $n=6$ term. Our value for Θ_D at 293 K is 666 K, so a rather rapid convergence behavior of Eq. (17) is expected.

The precision we give for B is 0.34% and is based on the least-squares results from the fits to the dispersion data with the BvK model. The variance relation used is

$$\sigma_B^2=\frac{\varepsilon}{No-Nv}\sum_{k\geqslant j}^{Nv}(2-\delta_{jk})(\partial B/\partial P_j)\varepsilon^{jk}(\partial B/\partial P_k), \tag{18}$$

where ε^{jk} are the inverse matrix elements of the least-squares matrix with ε at its minimum value. The first factor in Eq. (18) is χ^2 [cf. Eq. (8)] which is used to scale the variance of B to an observation of unit weight. The partial derivatives of B with respect to the force constants are listed in Table III. These were computed by numerical evaluation of B with small changes in the force constants. Notice that the partial derivatives of the diagonal elements of the force-constant matrices are negative, which is to be expected since an increase in a force constant lowers the root-mean-square amplitude of vibration. The more negative derivatives occur for μ'''' and λ'''', which are the diagonal elements of the sixth-nearest-neighbor force constants. Slightly larger than

TABLE III. Numerical derivatives of B with respect to force constants (m Å^2/N).

$\partial B/\partial\alpha$	−0.0241
$\partial B/\partial\beta$	0.0223
$\partial B/\partial\mu$	−0.0700
$\partial B/\partial\nu$	0.0187
$\partial B/\partial\lambda$	−0.0418
$\partial B/\partial\delta$	−0.0040
$\partial B/\partial\mu'$	−0.0937
$\partial B/\partial\nu'$	−0.0085
$\partial B/\partial\lambda'$	−0.0453
$\partial B/\partial\delta'$	0.0028
$\partial B/\partial\mu''$	−0.0514
$\partial B/\partial\lambda''$	−0.0237
$\partial B/\partial\mu'''$	−0.0904
$\partial B/\partial\nu'''$	0.0228
$\partial B/\partial\lambda'''$	−0.0505
$\partial B/\partial\delta'''$	0.0266
$\partial B/\partial\mu''''$	−0.2181
$\partial B/\partial\nu''''$	0.0060
$\partial B/\partial\lambda''''$	−0.1036
$\partial B/\partial\delta''''$	0.0190
$\partial B/\partial\gamma''''$	0.0164

−0.1 m Å^2/N are the partial derivatives of μ', a diagonal element of third-nearest-neighbor force constants and of μ''' which is the (1,1) and (2,2) element in the matrix for fifth-nearest neighbors. The $\sigma(B)$ determined from Eq. (18) with the derivatives given in Table III is 0.0016 Å^2. On the other hand, if *only* the diagonal terms ($k=j$) are used in Eq. (18), then the estimated standard deviation of B is 0.0746 Å^2. The caveat is to respect the off-diagonal elements in a least-squares matrix when the variables are not restricted to coefficients of orthogonal functions. For the case reported here, neglect of correlation terms gives an estimated standard deviation which is too large by nearly a factor of 50.

V. ANHARMONICITY IN SILICON

From the single-particle potential (1) proposed by Dawson and Willis, the authors of Ref. 19 showed that the structure factor for a diamond-type crystal has the functional form

$$F_{hkl}=8i^3b\exp(-M)(2\pi/a)^3(\beta_{\rm DW}/\alpha_{\rm DW}^3)(hkl)(k_BT)^2, \tag{19}$$

where b is the neutron-scattering length, a is the cubic cell length, $\alpha_{\rm DW}$ and $\beta_{\rm DW}$ are coefficients for the potential from Eq. (1) and M is the factor $B(\sin\theta/\lambda)^2$. The structure factor formula in Eq. (19) holds for that class of planes for which $h+k+l=4n+2$ and no h, k, or l is zero. The connection between B and $\alpha_{\rm DW}$ is, via Eq. (2),

$$B=\frac{8\pi^2k_BT}{\alpha_{\rm DW}10^{20}}$$

and $\alpha_{\rm DW}$ is scaled from J/m^2 to J/Å^2 by the factor of 10^{20}. From the results for $\langle u_{LD}^2\rangle$ in this work, $\alpha_{\rm DW}$ is 68.09

± 0.23 (N/m). This is the value to be used in the analysis of neutron structure factors for the anharmonic force constant β_{DW} by virtue of Eq. (19).

Besides the explicit T^2 dependence on the right-hand side of Eq. (19), M and a are also temperature dependent. M varies linearly with T [cf. Eq. (2)] and a has a very small dependence on T. These temperature-dependent factors are incorporated into the left-hand side of Eq. (19) and, after expressing $\sin\theta/\lambda$ in terms of a and h,k,l, Eq. (19) is rewritten as

$$\left(\frac{|F_{hkl}|}{hkl}\right)\left(\frac{a}{2\pi}\right)^3 \exp\left(\frac{2\pi^2 k_B T}{a^2 \alpha_{\mathrm{DW}} \times 10^{20}}(h^2+k^2+l^2)\right) = cT^2. \tag{20}$$

If $a(T)$ is known, one may use the left-hand side of Eq. (20) to construct reduced data R_{hkl} from the neutron structure factors. These R_{hkl}'s may be plotted against T^2 to determine c. A least-squares solution for c is

$$c = \sum_{n=1}^{No} wR_{hkl}T^2 \Big/ \sum_{n=1}^{No} wT^4. \tag{21}$$

The w are the inverse square errors reported for F_{hkl}. With a solution for c from Eq. (21), the estimated standard deviation is

$$\sigma(c) = \left(\frac{\Sigma_{n=1}^{No} w(R_{hkl} - cT^2)^2}{(No-1)\Sigma_{n=1}^{No} wT^4}\right)^{1/2}. \tag{22}$$

The sums in Eqs. (21) and (22) extend over the observed neutron structure factors, of which there are *No*.

The lattice parameter of silicon as a function of T from 300–1500 K, published by Okada and Tokumaru,[34] was used to construct the R_{hkl} [the left-hand side of Eq. (20)] along with the temperatures and neutron structure factors for (222), (442), and the (622) diffracting planes, given in Refs. 21 and 22. Altogether, 11 reflections made up *No* data used for the sums in Eq. (21). The value for c, from Eq. (21), is 3.723×10^{-9}, and its estimated standard deviation, via Eq. (22) is 5.4×10^{-11} in non-SI units of $\text{Å}^3\,\text{fm}\,\text{K}^{-2}$. A plot of R_{hkl} vs T^2 displays the fit of the reduced data to the temperature dependence predicted by the Dawson-Willis potential.[19]

The range of T was 288–1523 K for the plot in Fig. 3. a varied from 5.4309–5.4580 Å and the factor B in M varied from 0.4611–2.438 Å^2 over the temperature range that was used for the construction of R_{hkl}'s.

From $c = 8b(\beta_{\mathrm{DW}}/\alpha_{\mathrm{DW}}^3)k_B^2$, we extract the anharmonic parameter β_{DW}. The result is $18.58 \pm 0.27\ \text{N}\,\text{m}^{-1}\,\text{Å}^{-1}$ which are non-SI units that read newton per meter per angstørm. This result is about 75% of the average of the values in Table III of Tischler and Batterman.[7] This discrepancy is primarily due to the different values used for α_{DW}. Our value of 68.09 N/m is derived from $\langle u_{\mathrm{LD}}^2 \rangle$ but a value of 78.5 N/m was based on measurements of Θ_M done by Batterman and Chipman[35] and the approximation by Dawson and Willis[19] that the Debye function $\Phi(x_m) + x_m/4$ was essentially unity. Actually, at 300 K, the value is ≈ 1.08, but the use of unity does not account for the 15% difference.

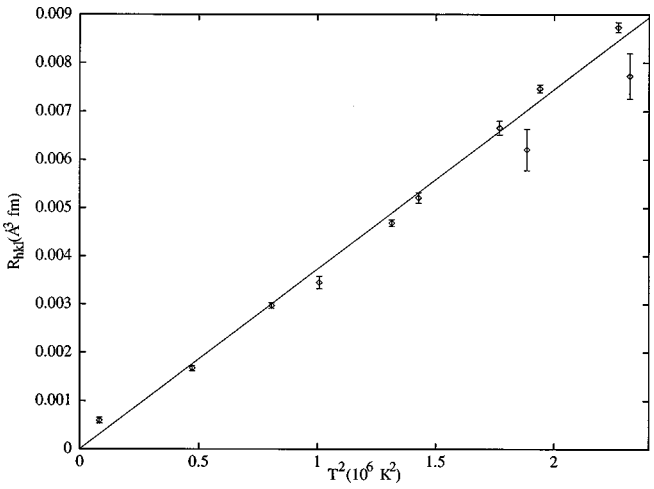

FIG. 3. Plot of R_{hkl} vs T^2.

VI. CONCLUSION

We have made a determination of the Debye-Waller factor in silicon at 293 K by lattice-dynamical methods. The essential feature was a fit to inelastic neutron-scattering data for special directions of the Brillouin zone with Born-von Kármán force constants, the BvK model. This is a phenomenological model which makes no prejudgement about the nature of the forces. One starts at a central atom and assigns undetermined force constants to successive atoms ''coupled'' to the central atom with no constraints other than ones that satisfy the symmetry properties of normal vibrations in a crystal.[36,37] The effective potential for the nuclear motion is assumed to be due to an electronic system that remains in its adiabatic ground state. For a crystal of the diamond structure, there are two sublattices of the atoms; one centered at the site [0, 0, 0] and the other at $(a/4)[1, 1, 1]$, where a is the cubic lattice cell length. The BvK force constant matrices are arranged in a series of shells which are labeled by the ordinal numbers 1st, 2nd,... nearest neighbors. It is often tacitly assumed that the relative importance of the force constant matrices decrease with increasing distance between the atoms. This is decidedly not the case as first suggested by Herman[18] and illustrated by actual fits to dispersion data.[17] Our results are based on 21 BvK force constants derived from the first six-nearest-neighbor force constant matrices. Truncation of the BvK expansion necessarily introduces a systematic error of some sort, but it is difficult to quantify with the present information. The figure of merit for quality of fit R_w (6) changes from 2.81–2.54% with a change from fifth-nearest neighbors (sixteen disposable force constants) to our ''complete'' set of 21 BvK constants. The corresponding values for B are 0.470 and 0.469 Å^2, respectively. By contrast, a second-nearest-neighbor fit has an R_w of 14.2%, the force constants of which predict a B of 0.53 Å^2. The truncation at 2 compared to 5 or 6 has a systematic error of 13%, while the difference between fifth- and sixth-nearest neighbor differ in B values by about 0.2%. The omission of force constants beyond second nearest neighbors predicts a much ''softer'' crystal with a mean-square amplitude of vibration that is more than 12% larger than for the real crystal of silicon at 293 K. The near agreement of B values based on fifth- or sixth-nearest neighbor

BvK force constants does not guarantee that our results have converged to the correct lattice-dynamical value with a systematic error less than two or three parts per thousand. Inclusion of seventh- and eighth-nearest neighbors would extend the list of disposable force constant parameters to 29 in the least-squares fitting of the phonon dispersion data. In the absence of more inelastic neutron-scattering measurements, the degrees of freedom would be reduced to 164 and an overdetermination ratio No/Nv of 6.7 compared to the present ratio of 9.2. The lattice-dynamically derived value for B probably has an accuracy of four parts per thousand or better. We leave the matter here and turn to a discussion comparing the value of B derived in this work to other experimental estimates.

The thermal mean-square amplitude of vibration $\langle u^2_{\rm Neu}\rangle$ derived from neutron powder-diffraction data[12] is $0.0059 \pm 0.0002_5$ Å^2 when scaled from 284–293 K, which agrees with the result here, albeit a far less precise value. Recall that $\langle u^2_{\rm LD}\rangle$ is $0.005\,941 \pm 0.000\,021$ Å^2. A number of B values for silicon, derived from x-ray-diffraction measurements are reported in the literature. In a study of the electron-density distribution in silicon by Spackman,[9] where concern for the nature of the core scattering was addressed, an average value for $\langle u^2_{\rm xray}\rangle$ equal to $0.005\,866 \pm 0.000\,014$ Å^2 was reported. The average was based on x-ray-diffraction data from Ag $K\alpha$ and Mo $K\alpha$ radiation. The x-ray structure factors were taken from measurements in a temperature range from 293–298 K as cited in Ref. 9. In comparing to our value at 293 K, the range for $\langle u^2_{\rm xray}\rangle$ has a systematic uncertainty of $\pm 0.000\,099$ Å^2 if the temperature for the x-ray Debye-Waller factor is taken as 295.5 ± 2.5 K. Notice that the temperature range introduces a spread for $\langle u^2_{\rm xray}\rangle$ that is about seven times the quoted estimated standard deviation. In any event, the x-ray value is *very* close to the lattice-dynamical value. For the results presented here, there is little or no evidence of a systematic difference due to an erroneous Si x-ray-scattering factor or to an incomplete expansion of BvK force constants.

With the use of a single-particle potential, proposed by Dawson and Willis, an anharmonic force constant has been extracted from the temperature dependent neutron structure factors measured by Batterman and co-workers.[20–22] The result for $\beta_{\rm DW}$ is *critically* dependent upon the choice for $\alpha_{\rm DW}$. In a paper on the (222) ''forbidden'' reflection, Keating *et al.*[20] use a value of 78.5 N/m for $\alpha_{\rm DW}$ which is taken from the paper by Dawson and Willis[19] who set the Debye function to unity in order to get an estimate of the isotropic force constant from Θ_M. The temperature dependence of x-ray-diffraction intensities from powder samples of silicon was used by Batterman and Chipman to determine Θ_M. An average value of 543 ± 8 K for silicon was reported in Ref. 35. Our lattice-dynamical value for Θ_M is 527 K. The slopes of the temperature plots done by Batterman and Chipman are proportional to Θ_M^{-2} so the difference in slopes amounts to a factor of 1.06 and implies that a value of 72.3 N/m for $\alpha_{\rm DW}$ is more compatible with the Batterman and Chipman value for Θ_M. If 72.3 N/m is used for the isotropic force constant in the Dawson-Willis potential function with the same data and analysis as done in this paper, $\beta_{\rm DW}$ is 21.9 N m^{-1} Å^{-1} in contrast to the lattice-dynamically based value of 18.58. The actual value for the anharmonic force constant in the Dawson-Willis potential is strongly dependent on the choice of the isotropic force constant rather than the reduced neutron data given in Eq. (20).

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