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Anharmonic contributions to the Debye-Waller factor: Calculation and application to aluminum

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We have presented a method for an exact calculation of the quasiharmonic (which allows for the volume dependence of the phonon frequencies) and the two lowest-order, cubic and quartic, anharmonic contributions to the Debye-Waller factor (DWF) or atomic mean-square displacement of an anharmonic crystal in the high-temperature limit. Although the method is applicable to any monatomic cubic crystal, specific results are presented for a nearest-neighbor central-force model of a fcc crystal for any two-body potential $\phi(r)$. The method requires a knowledge of seven Brillouin-zone (BZ) sums and the first four potential derivatives of $\phi(r)$ evaluated at the nearest-neighbor distance appropriate for the temperature T K. The BZ sums are calculated to a high degree of accuracy and presented for a ratio parameter a_1, which depends on the first and second derivatives of $\phi(r)$, in the range $0 \leq a_1 \leq 0.1$ in steps of 0.02. We have also presented a highly accurate exponential fit for each of the seven BZ sums. The argument of the exponential is a polynomial of degree 5 in the variable a_1. We have applied this method to the calculation of the DWF for Al using a three-parameter and a four-parameter Morse potential function. We have also assessed the validity of the leading-term approximation introduced earlier, in such calculations, by Maradudin and Flinn. Introduction of this approximation gives a negative anharmonic contribution to the DWF. The exact calculation gives a positive contribution. We have also performed calculations with the Harrison modified point-ion pseudopotential with 13 neighbors in the harmonic interaction and 8 neighbors in the anharmonic interaction at 0 K volume. A comparison of the theoretical results of the DWF with their experimental values in Al shows that the agreement with experiment is good up to 500 K. The theory and experiment differ by 16% at the highest temperature, 900 K. We ascribe this difference to the limited applicability of the Morse potential and the fixed volume dependence of the pseudopotential.

I. INTRODUCTION

Since the first calculation of the lowest-order anharmonic contributions to the atomic mean-square displacement $\langle u^2 \rangle$ or the Debye-Waller factor (DWF) by Maradudin and Flinn,[1] which was done in the leading-term approximation for a nearest-neighbor central-force (NNCF) model of a fcc crystal, many exact calculations of $\langle u^2 \rangle$ of DWF have been reported in the literature.[2-5] For example, $\langle u^2 \rangle$ or DWF has been calculated for *all* the bcc alkali metals by Shukla and Mountain[2] and Shukla and Heiser.[3] These authors employed a long-range sixth-neighbor interaction potential derived from a pseudopotential theory. The adequacy of the lowest-order (λ^2) perturbation theory (PT) was tested[2,3] by comparing the $\langle u^2 \rangle$ results with those of the molecular-dynamics (MD) method for the same potential function because the latter method presumably includes *all* anharmonic contributions. The results for $\langle u^2 \rangle$ by both methods agreed quite well, and thereby showed the adequacy of the λ^2 PT for the alkali metals. For short-range interactions, such as the 12-6 Lennard-Jones (12-6 LJ) potential applied to the NNCF model of the fcc crystal, $\langle u^2 \rangle$ was calculated by Heiser, Shukla, and Cowley[4] by the λ^2 PT, MD, and the Monte-Carlo (MC) method, which also gives all anharmonic contributions. This calculation demonstrated the adequacy of the λ^2 PT only up to $\frac{3}{4}$ of the melting temperature (T_m). More recently it has been shown by Shukla and Hübschle[5] that the MC results for $\langle u^2 \rangle$ can be adequately represented up to T_m for the 12-6 LJ NNCF model of the fcc crystal when the anharmonic calculations of $\langle u^2 \rangle$ are carried out by a Green's function method.

Clearly, the methods used in the above calculations[2-5] of $\langle u^2 \rangle$, as well as an earlier calculation by Wolfe and Goodman[6] for a model of a fcc Cu crystal, are geared to a particular potential and a range of neighbor interactions.

However, it is possible to carry out an exact calculation of the anharmonic properties for a model of a fcc or bcc crystal and present the final results in a form which is applicable to any short-range model potential. This type of exact calculation of the lowest-order anharmonic contributions to the Helmholtz free energy F, which is fundamental in the calculation of the equation of state, has been carried out for the NNCF model of the fcc crystal[7,8] and the nearest and next-nearest (NNNCF) model of the bcc crystal.[9,10] The final results are expressed in terms of potential derivatives and a certain number of Brillouin zone (BZ) sums which are tabulated as a function of a parameter a_1. The parameter a_1 depends on the first and second derivatives of a two-body potential $\Phi(r)$ and characterizes the volume dependence of the BZ sums.

The Helmholtz free energy to $O(\lambda^2)$ and $O(\lambda^4)$ (where λ is the Van Hove perturbation expansion parameter) of the above fcc model has been calculated by Shukla[7] and Shukla and Wilk,[8] and Shukla and Cowley,[11] respectively. The equation-of-state results have been obtained for the Lennard-Jones, Morse and Rydberg potentials in rare-gas solids[12] employing the λ^4 PT and Morse and Rydberg potentials for several fcc metals[13,14] for the λ^2 PT. For the above bcc crystal model the free energy and the equation of state results for the λ^2 PT have been obtained by MacDonald, Shukla and Kahaner[9] for the alkali metals and by MacDonald and Shukla[10] for the transition metals.

A similar exact calculation of the anharmonic contributions to $\langle u^2 \rangle$ has not been carried out although it would be worthwhile to do so. $\langle u^2 \rangle$ enters in the calculation of the Debye-Waller factor (DWF) which appears in the temperature dependence of the intensity of the Bragg x-ray and elastic neutron scattering and in the Mössbauer fraction. It also is important in theories of melting based on the Lindemann criterion.

The objective of this paper is to develop an algebraic method from which exact numerical results for the harmonic and anharmonic (cubic and quartic) contributions to $\langle u^2 \rangle$ can be obtained for any $\Phi(r)$ like the Lennard-Jones, Morse, Rydberg, and other model short-range potentials. The method presented in this paper for the anharmonic calculation of $\langle u^2 \rangle$ is similar in spirit to that of the calculation of F. The algebraic expressions for the harmonic and anharmonic contributions to $\langle u^2 \rangle$ are derived for the NNCF interaction model of the fcc crystal. The expressions contain a number of BZ sums which depend on a_1, and the potential derivatives of $\Phi(r)$. From these expressions $\langle u^2 \rangle$ can be calculated at any temperature (T) and volume (V). Although the method is applicable only to the NNCF model of a fcc crystal, it is valid for any $\Phi(r)$ such as those obtained from pseudopotential theory, but only in approximation.

As mentioned earlier, the first calculation of the DWF or $\langle u^2 \rangle$ was carried out by Maradudin and Flinn[1] for a NNCF model of the fcc crystal. The harmonic and the lowest order (cubic and quartic) anharmonic contributions to DWF were evaluated by these authors in the leading-term approximation. How good this approximation is in the calculation of $\langle u^2 \rangle$ is not known. Because the results obtained by Maradudin and Flinn have been used by several workers,[15–17] it will be useful to assess the validity of the leading-term approximation (LTA). The present work will assess the validity of LTA.

In Sec. II we present a summary of the high-temperature ($T > \Theta_D$, Θ_D is the Debye temperature) expressions for the harmonic and the two lowest-order (λ^2) anharmonic contributions to $\langle u^2 \rangle$ and the details of their calculation. In Sec. III we present the final expressions which can be used for the calculation of any $\phi(r)$. The LTA is discussed in Sec. IV. The results and discussion are presented in Sec. V. The conclusion of this work is presented in Sec. VI.

II. CALCULATION OF THE DEBYE-WALLER FACTOR (DWF)

Maradudin and Flinn[1] have derived the high-temperature limit expressions for the anharmonic contributions to DWF in the lowest order (λ^2) of perturbation theory by retaining the cubic and quartic terms in the Hamiltonian. They found four anharmonic contributions: two of these were isotropic and proportional to $|\mathbf{q}|^2$ ($\mathbf{q}$ is the wave vector) and the other two were nonisotropic and proportional to $|\mathbf{q}|^4$. They evaluated both isotropic contributions in the leading-term approximation and the two anisotropic contributions in the Ludwig and the leading-term approximations for a NNCF model of a fcc crystal. A test of the validity of these approximations in DWF calculations has not been reported in the literature. In the context of Helmholtz free-energy calculations, the leading-term approximation has been shown to be poor.[8]

In order to present our calculations clearly for any $\phi(r)$ and a cubic crystal it is necessary to present here the basic expressions for the harmonic and anharmonic contributions to DWF. In the classical high-temperature limit ($T > \Theta_D$), these contributions can be obtained from Maradudin and Flinn.[1] We represent the harmonic contributions, or more appropriately with volume dependence of phonon frequencies the quasiharmonic (QH) contribution to DWF by $2M_{\mathrm{QH}}(\mathbf{q})$, and two isotropic λ^2 contributions to DWF by $2M_1(\mathbf{q})$ and $2M_2(\mathbf{q})$. Expressions appropriate for cubic crystals are summarized here from Shukla and Mountain.[2] These are given by

$$2M_{\mathrm{QH}}(\mathbf{q}) = \frac{|\mathbf{q}|^2 (k_B T)}{3NM} \sum_{\mathbf{q}_1 j_1} \frac{1}{\omega^2(\mathbf{q}_1 j_1)} , \tag{1}$$

$$2M_1(\mathbf{q}) = -|\mathbf{q}|^2 \frac{(k_B T)^2}{6N^2 M} \sum_{\mathbf{q}_1 \mathbf{q}_2} \sum_{j_1 j_2} \frac{\Phi(\mathbf{q}_1 j_1, -\mathbf{q}_1 j_1, \mathbf{q}_2 j_2, -\mathbf{q}_2 j_2)}{\omega^2(\mathbf{q}_1 j_1)\,\omega^4(\mathbf{q}_2 j_2)} , \tag{2}$$

$$2M_2(\mathbf{q}) = |\mathbf{q}|^2 \frac{(k_B T)^2}{6N^2 M} \sum_{\mathbf{q}_1 \mathbf{q}_2 \mathbf{q}_3} \sum_{j_1 j_2 j_3} \Delta(\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{q}_3) \frac{\Phi(\mathbf{q}_1 j_1, \mathbf{q}_2 j_2, \mathbf{q}_3 j_3)\,\Phi(-\mathbf{q}_1 j_1, -\mathbf{q}_2 j_2, -\mathbf{q}_3 j_3)}{\omega^2(\mathbf{q}_1 j_1)\,\omega^2(\mathbf{q}_2 j_2)\,\omega^4(q_3 j_3)} . \tag{3}$$

The various symbols appearing in Eqs. (1)–(3) have the following meaning: M is the atomic mass, k_B is the Boltzmann constant, T is the temperature, and N represents the number of unit cells in the crystal. The delta function $\Delta(\mathbf{q}_1 + \mathbf{q}_2 + \cdots + \mathbf{q}_n)$ appearing in Eq. (3) is unity if $(\mathbf{q}_1 + \mathbf{q}_2 + \cdots + \mathbf{q}_n)$ is zero or a vector of the reciprocal lattice (τ) and zero otherwise. The Φ functions appearing in Eqs. (1) and (2) are the Fourier transforms of the third- and fourth-order atomic force constants. In general, the Fourier transform of the nth-order tensor atomic force constant $\phi_{\alpha\beta\cdots\mu}(l)$

is defined by the following:

$$\Phi(\mathbf{q}_1j_1,\mathbf{q}_2j_2,\ldots,\mathbf{q}_nj_n)=\frac{1}{2M^{n/2}}\sum_l{}'\sum_{\alpha\beta\cdots\mu}\phi_{\alpha\beta\cdots\mu}(l)\times\varepsilon_\alpha(\mathbf{q}_1j_1)\cdots\varepsilon_\mu(\mathbf{q}_nj_n)(1-e^{i\mathbf{q}_1\cdot\mathbf{r}_l})(1-e^{i\mathbf{q}_2\cdot\mathbf{r}_l})\cdots(1-e^{i\mathbf{q}_n\cdot\mathbf{r}_l})\ , \qquad (4)$$

where the prime over the direct lattice vector (l) summation in the previous equation indicates the omission of the origin point, and $\omega(\mathbf{q}j)$ and $\varepsilon(\mathbf{q}j)$ are the eigenvalues and eigenvectors, respectively, for the wave vector $\mathbf{q}$ and branch index j.

Substituting for $\Phi(\mathbf{q}_1j_1,-\mathbf{q}_1j_1,\mathbf{q}_2j_2,-\mathbf{q}_2j_2)$ from Eq. (4) into Eq. (2) we can separate the BZ sums over $\mathbf{q}_1$ and $\mathbf{q}_2$ and branch index summations (j_1 and j_2) in terms of the two basic tensors

$$S_{\alpha\beta}(l)=\sum_{\mathbf{q}j}\frac{\varepsilon_\alpha(\mathbf{q}j)\varepsilon_\beta(\mathbf{q}j)}{\omega^2(\mathbf{q}j)}\cos(\mathbf{q}\cdot\mathbf{r}_l)\ , \qquad (5)$$

$$T_{\gamma\delta}(l)=\sum_{\mathbf{q}j}\frac{\varepsilon_\gamma(\mathbf{q}j)(\varepsilon_\delta(\mathbf{q}j)}{\omega^4(\mathbf{q}j)}\cos(\mathbf{q}\cdot\mathbf{r}_l)\ , \qquad (6)$$

which can be numerically evaluated, for any direct lattice vector $\mathbf{r}_l$ by transforming the whole BZ sum appearing in the right-hand side of Eqs. (5) and (6) to that over the ($\frac{1}{48}$) portion of the irreducible section of BZ. The transformed equations for the diagonal and off-diagonal elements of $S_{\alpha\beta}$ are derived in Shukla and Wilk.[8] $T_{\gamma\delta}$ can be obtained in a similar manner.

In terms of the above tensors, $2M_1(\mathbf{q})$ can be written as

$$2M_1(\mathbf{q})=-|\mathbf{q}|^2\frac{(k_BT)^2}{24B^3(r_0)}\times\sum_l{}'\sum_{\alpha\beta}\sum_{\gamma\delta}\phi_{\alpha\beta\gamma\delta}(l)[S_{\alpha\beta}(0)-S_{\alpha\beta}(l)]\times[T_{\gamma\delta}(0)-T_{\gamma\delta}(l)]\ , \qquad (7)$$

where the factor $B^3(r_0)$ in Eq. (7) arises from scaling of $\omega(\mathbf{q}j)$ to their dimensionless form $\lambda(\mathbf{q}j)$ via the equation $\omega^2(\mathbf{q}j)=[2B(r_0)/M]$. $B(r_0)$ is the value of $B(r_l)$ at the nearest-neighbor distance (r_0) and is defined later.

The calculation of $2M_2(\mathbf{q})$ is not so simple because of the Δ function contained in Eq. (2). However, the three BZ and branch index summations can be separated by introducing the following plane-wave representation of the Δ function:

$$\Delta(\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3)=\frac{1}{N}\sum_l\exp[i(\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3)\cdot\mathbf{r}_l]\ . \qquad (8)$$

Once again substituting for $\Phi(\mathbf{q}_1j_1,\mathbf{q}_2j_2,\mathbf{q}_3j_3)$ from Eq. (4) into Eq. (3) and using the representation (8) for Δ we can express $2M_2(\mathbf{q})$ in terms of $S_{\alpha\beta},T_{\gamma\delta}$ tensors. The final form arrived at is

$$\begin{aligned}2M_2(\mathbf{q})=|\mathbf{q}|^2\frac{(k_BT)^2}{192B^4(r_0)}\sum_l\sum_{l_1}{}'\sum_{l_2}{}'\sum_{\alpha\beta\gamma}\sum_{\lambda\mu\nu}{}'\phi_{\alpha\beta\gamma}(l_1)\phi_{\lambda\mu\nu}(l_2)&[S_{\alpha\lambda}(l)-S_{\alpha\lambda}(l-l_1)-S_{\alpha\lambda}(l-l_2)+S_{\alpha\lambda}(l-l_1+l_2)]\\&\times[S_{\beta\mu}(l)-S_{\beta\mu}(l-l_1)-S_{\beta\mu}(l-l_2)+S_{\beta\mu}(l-l_1+l_2)]\\&\times[T_{\gamma\nu}(l)-T_{\gamma\nu}(l-l_1)-T_{\gamma\nu}(l-l_2)+T_{\gamma\nu}(l-l_1+l_2)]\end{aligned} \qquad (9)$$

where the sum over l is over *all* direct lattice points and l_1,l_2 are restricted to the neighbor sums of the lattice under consideration.

The quasiharmonic contribution to DWF can also be evaluated from the diagonal elements of the tensor $S_{\alpha\beta}(l)$ evaluated at $l=0$, i.e.,

$$2M_{\mathrm{QH}}(\mathbf{q})=\frac{|\mathbf{q}|^2(k_BT)}{3NM}[S_{xx}(0)+S_{yy}(0)+S_{zz}(0)]\ . \qquad (10)$$

Equation (10) is equivalent to Eq. (1) because of the normalization property of the eigenvectors.

At this point in the calculation the only things left to be spelled out in the calculation of $2M_1(\mathbf{q})$ and $2M_2(\mathbf{q})$ are $\phi_{\alpha\beta\gamma}(l)$ and $\phi_{\alpha\beta\gamma\delta}(l)$. We present here complete expressions for these tensors for the exact calculations of $2M_1(\mathbf{q})$ and $2M_2(\mathbf{q})$ as well as for the discussion of the leading-term approximation. For any $\phi(r)$, these expressions are given by

$$\phi_{\alpha\beta\gamma}(l)=\frac{\alpha_l\beta_l\gamma_l}{r_l^3}C(r_l)+(\alpha_l\delta_{\beta\gamma}+\beta_l\delta_{\gamma\alpha}+\gamma_l\delta_{\alpha\beta})\frac{B(r_l)}{r_l^2}\ , \qquad (11)$$

$$\begin{aligned}\phi_{\alpha\beta\gamma\delta}(l)=&\frac{\alpha_l\beta_l\gamma_l\delta_l}{r_l^4}D(r_l)\\&+(\alpha_l\beta_l\delta_{\gamma\delta}+\beta_l\gamma_l\delta_{\alpha\delta}+\alpha_l\gamma_l\delta_{\beta\delta}\\&+\alpha_l\delta_l\delta_{\beta\gamma}+\beta_l\delta_l\delta_{\alpha\gamma}+\gamma_l\delta_l\delta_{\alpha\beta})\frac{C(r_l)}{\gamma_l^3}\\&+(\delta_{\alpha\beta}\delta_{\gamma\delta}+\delta_{\beta\gamma}\delta_{\alpha\delta}+\delta_{\alpha\gamma}\delta_{\beta\delta})\frac{B(r_l)}{r_l^2}\ ,\end{aligned} \qquad (12)$$

where $\alpha,\beta,\gamma,\delta$ are each assigned the values of x,y,z, respectively, and α_l, β_l, etc. are the corresponding components of the direct lattice vector $\mathbf{r}_l$. B,C,D are combinations of derivatives of $\phi(r)$ evaluated at $r_l=|\mathbf{r}_l|$.

These are defined as

$$B(r_l)=\left[\phi''(r)-\frac{1}{r}\phi'(r)\right]_{r=r_l}, \tag{13}$$

$$C(r_l)=\left[\phi'''(r)-\frac{3}{r}\phi''(r)+\frac{3}{r^2}\phi'(r)\right]_{r=r_l}, \tag{14}$$

$$D(r_l)=\left[\phi^{\text{iv}}(r)-\frac{6}{r}\phi'''(r)+\frac{15}{r^2}\phi''(r)-\frac{15}{r^3}\phi'(r)\right]_{r=r_l}. \tag{15}$$

There are convergence problems in the numerical evaluation of $S_{\alpha\beta}(l)$ and $T_{\gamma\delta}(l)$. $T_{\gamma\delta}(l)$ converges much more slowly than $S_{\alpha\beta}(l)$ for any choice of the mesh size. This is due to $\omega^4(\mathbf{q}_j)$ in the denominator of Eq. (6). We have used a simple cubic mesh to fill the $\frac{1}{48}$ portion of the irreducible section of BZ, viz, $|q_x|+|q_y|+|q_z| \leq \frac{3}{2}$, $1\geq|q_x|\geq|q_y|\geq|q_z|\geq 0$, say, for a fcc lattice. It does not matter how many points are used in the calculation, the convergence of individual tensors $T_{\gamma\delta}$ remain slow compared to $S_{\alpha\beta}$. The weighting (or contributions) from points close to $\mathbf{q}\cong 0$ is important. However, what enters in the calculation of $2M_1(\mathbf{q})$ and $2M_2(\mathbf{q})$ is the difference of these tensors which converges much better than the individual tensors. The problem remains in the calculation of $2M_{\text{QH}}(\mathbf{q})$. To solve these convergence problems we used a graphical extrapolation procedure in our calculations. After computing these quantities for a large number of step lengths (L), a graph was plotted versus $1/L$ and extrapolated to a step length corresponding to $L\rightarrow\infty$. The above method is valid for the DWF calculation of any monatomic cubic lattice (sc, bcc, and fcc). In the next section we specialize it for the NNCF model of the fcc crystal.

III. EXPRESSIONS FOR $2M_1(\mathbf{q})$, $2M_2(\mathbf{q})$, AND $2M_{\text{QH}}$ FOR A NNCF MODEL OF A fcc LATTICE

We substitute Eq. (12) into Eq. (7) and Eq. (11) into Eq. (9). After some lengthy algebraic manipulations the equations for $2M_1(\mathbf{q})$ and $2M_2(\mathbf{q})$ can be reduced to the following form for application to any $\phi(r)$:

$$2M_1(\mathbf{q})=-\frac{|\mathbf{q}|^2(k_BT)^2}{3B^3(r_0)}\left[D(r_0)S_{4A}(a_1)+\frac{C(r_0)}{r_0}S_{4B}(a_1)+\frac{B(r_0)}{r_0^2}S_{4C}(a_1)\right], \tag{16}$$

$$2M_2(\mathbf{q})=\frac{|\mathbf{q}|^2(k_BT)^2}{F^4(r_0)}\left[C^2(r_0)S_{3A}(a_1)+\frac{2B(r_0)C(r_0)}{r_0}S_{3B}(a_1)+\frac{B^2(r_0)}{r_0^2}S_{3C}(a_1)\right], \tag{17}$$

$$2M_{\text{QH}}=\frac{|\mathbf{q}^2|3k_BT}{6B(r_0)}S_{\text{QH}}(a_1), \tag{18}$$

where in the above equations $B(r_0)$, $C(r_0)$, and $D(r_0)$ are evaluated from Eqs. (13)–(15) at the nearest-neighbor distance corresponding to temperature T and the BZ sums S_{4A},S_{4B},S_{4C}; S_{3A},S_{3B},S_{3C}; and S_{QH} are evaluated at the same temperature for the ratio $a_1=\phi'(r_0)/[r_0\phi''(r_0)-\phi'(r_0)]$. $F(r_0)=\phi''(r_0)+(1/r_0)\phi'(r_0)$. These sums are presented in Tables I–III as a function of a_1.

From these tables, one can either interpolate the value of these sums for a_1, whose value lies in between the intervals given for a_1, or some fitted functional form can be used. In Table IV we present the coefficients of one such fitted functional form, viz., $f(a_1)=\exp[P(a_1)]$, where $P(a_1)=\sum_{n=0}^{5}b_n(a_1)^n$, for each of the seven BZ sums. These fits reproduce the numerical values of the BZ sums almost exactly.

IV. LEADING-TERM APPROXIMATION (LTA)

As mentioned in the Introduction, the results of DWF, first derived by Maradudin and Flinn, have been used extensively by several workers in the past. This approximation amounts to only retaining the highest-ordered radial derivative in the Cartesian tensors $\phi_{\alpha\beta\gamma}$ and $\phi_{\alpha\beta\gamma\delta}$. Thus from Eqs. (11) and (12) we get

$$\phi_{\alpha\beta\gamma}(l)\cong\frac{\alpha_l\beta_l\gamma_l}{r_l^3}\phi'''(r_l), \tag{19}$$

TABLE I. Dimensionless sum S_{QH} for different values of a_1.

a_1	S_{QH}
0.10	0.588 17
0.08	0.624 69
0.06	0.666 52
0.04	0.714 97
0.02	0.771 91
0.00	0.840 01

TABLE II. Dimensionless sums, S_{4A},S_{4B},S_{4C} for different values of a_1.

a_1	S_{4A}	S_{4B}	S_{4C}
0.10	0.116 319	1.342 787	2.756 750
0.08	0.137 603	1.599 144	3.328 538
0.06	0.164 875	1.930 325	4.079 325
0.04	0.200 566	2.367 725	5.088 750
0.02	0.248 484	2.960 975	6.485 275
0.00	0.314 891	3.792 513	8.486 788

TABLE III. Dimensionless sums S_{3A}, S_{3B}, S_{3C} for different values of a_1.

a_1	S_{3A}	S_{3B}	S_{3C}
0.10	0.028 267 4	0.098 027 8	0.544 704
0.08	0.030 714 2	0.106 085	0.592 583
0.06	0.033 761 6	0.116 088	0.652 358
0.04	0.037 642 4	0.128 779	0.728 713
0.02	0.042 719 8	0.145 308	0.829 022
0.00	0.049 590 0	0.167 553	0.965 503

$$\phi_{\alpha\beta\gamma\delta}(l) \cong \frac{\alpha_l \beta_l \gamma_l \delta_l}{r_l^4} \phi^{\text{iv}}(r_l) , \tag{20}$$

and

$$B(r_l) \cong \phi''(r_l) . \tag{21}$$

The expressions for $2M_1(\mathbf{q})$, $2M_2(\mathbf{q})$, and $2M_{\text{QH}}(\mathbf{q})$ in the LTA simplify to

$$2M_1(\mathbf{q}) = -\frac{|\mathbf{q}|^2 (k_B T)^2 \phi^{\text{iv}}(r_0)}{3[\phi''(r_0)]^3} S_{4A}^{\text{LTA}} , \tag{22}$$

$$2M_2(\mathbf{q}) = \frac{|\mathbf{q}|^2 (k_B T)^2 [\phi'''(r_0)]^2}{[\phi''(r_0)]^4} S_{3A}^{\text{LTA}} , \tag{23}$$

$$2M_{\text{QH}}(\mathbf{q}) = \frac{|\mathbf{q}|^2 3 k_B T}{6[\phi''(r_0)]} S_{\text{QH}}^{\text{LTA}} , \tag{24}$$

where in obvious notation we have put the superscript LTA in the three BZ sums S_{4A}, S_{3A}, and S_{QH}, respectively. All these sums are evaluated at $a_1 = 0$.

In the calculation of $2M_{\text{QH}}(\mathbf{q})$ the volume dependence comes from the BZ sum S_{QH} and the B factor in the denominator in Eq. (18). Maradudin and Flinn did not allow the variation of S_{QH} with volume, but B was allowed to vary with volume. In introducing the LTA first $B(r)$ was approximated, as given by Eq. (21), and then expanded in powers of ϵ where $r = r_0(1+\epsilon)$. ϵ was determined by minimizing the sum of the quasiharmonic free energy (also evaluated in LTA) and the static energy. This procedure led to an extra term in $2M_{\text{QH}}$ proportional to $(k_B T)^2$. However, this procedure of evaluating $2M_{\text{QH}}$ is inconsistent because of the neglect of the volume dependence of S_{QH}. As shown in Shukla and MacDonald,[13] the volume dependences of B and S_{QH} act in opposite directions, at least in the calculation of ε. We discuss the numerical results obtained from LTA in Sec. V.

V. RESULTS AND DISCUSSION

The quasiharmonic and λ^2 PT contributions to $\langle u^2 \rangle$ have been calculated at different temperatures and appropriate zero-pressure volumes by Heiser, Shukla, and Cowley[4] (HSC) for the NNCF model of a fcc lattice with the 12-6 Lennard-Jones potential. An obvious test of the method presented in this paper is to calculate these contributions to $\langle u^2 \rangle$ from Eqs. (16)–(18) and the BZ sums presented in Tables I–IV for the above potential. We have done these calculations and found that they agree quite well with those of HSC with some minor differences because the cubic contribution as calculated by HSC was not fully converged.

Next we apply this method to the calculation of DWF for Al between 300 and 900 K for two types of NNCF Morse potential functions: the usual function with three parameters whose values were determined in our earlier work[13] and a modified form introduced by MacDonald and MacDonald.[14] The latter form has an extra parameter (b) which is determined by calculating the thermal expansion $\varepsilon(T)$ for several values of b and then requiring that the initial slope near $T = \Theta_D$ be in agreement with the experimental values. In both calculations of DWF we have included the exact volume dependence of the harmonic and anharmonic contributions by employing Eqs. (16)–(18) and the BZ sums presented in Tables I–IV.

The volume dependence comes from the BZ sums and the derivatives B, C, D defined in Eqs. (13)–(15), each of which have to be evaluated at the appropriate $r(T)$. The values of $r(T)$ are the same as determined in the previous work[13,14] by minimizing the total energy of the system for these potentials. This total energy consists of the static energy plus the harmonic and λ^2 anharmonic (cubic and quartic) contributions to the Helmholtz function.

We have also made these calculations for the Harrison modified point-ion pseudopotential[18] which was used in our earlier work on the specific heat of Al.[19] But this calculation of DWF is done for a fixed volume (0 K volume). This is a long-range potential which required considering 13 neighbors in the harmonic interaction (for the calculation of phonon frequencies) and 8 neighbors in the anhar-

TABLE IV. Coefficients of the least-squares fit of the functions $S_{\text{QH}}(a_1)$, etc., each fitted to the form $y = \exp[P(a_1)]$, where $P(a_1) = \sum_{n=0}^{5} b_n (a_1)^n$.

	b_0	b_1	b_2	b_3	b_4	b_5
S_{QH}	−0.174 341	−4.454 94	12.2157	−44.1948	126.459	−151.237
S_{4A}	−1.155 53	−12.4982	35.4259	−141.374	514.150	−1037.31
S_{4B}	1.333 03	−13.0698	37.5063	−150.333	554.644	−1150.08
S_{4C}	2.138 51	−14.2170	41.4864	−165.353	596.810	−1195.17
S_{3A}	−3.003 97	−8.123 96	36.3668	−160.682	593.867	−1205.75
S_{3B}	−1.786 46	−7.763 36	34.9417	−155.390	583.985	−1213.79
S_{3C}	−0.035 106	−8.315 11	37.9244	−170.970	636.612	−1283.05

TABLE V. Temperature dependence of Debye-Waller factor (B) for aluminum in units of Å^2.

Temp (K)		300	400	500	600	700	800	900
Morse 1 QH[a]		0.832	1.123	1.421	1.727	2.042	2.366	2.700
	$C+Q$[b]	0.015	0.027	0.042	0.062	0.084	0.112	0.144
Morse 2 QH		0.863	1.177	1.506	1.852	2.215	2.597	2.998
	$C+Q$	0.004	0.007	0.010	0.013	0.016	0.018	0.018
Morse 1 QH		0.800	1.066	1.333	1.600	1.866	2.133	2.400
	$C+Q$ (0 K vol.)	0.015	0.026	0.040	0.058	0.079	0.103	0.131
LTA	QH	0.857	1.168	1.492	1.830	2.180	2.544	2.920
	$C+Q$	−0.022	−0.061	−0.061	−0.088	−0.119	−0.156	−0.197
Harrison QH		0.732	0.976	1.220	1.464	1.708	1.952	2.196
	$C+Q$ (0 K vol.)	0.043	0.076	0.118	0.170	0.232	0.303	0.383

[a] Quasiharmonic.

[b] Cubic and quartic.

monic (cubic and quartic) interactions. This calculation of DWF required employing Eqs. (1)–(4).

In order to assess the validity of LTA, described in Sec. IV, we have made the calculations for the three-parameter Morse potential at the fixed 0 K volume.

The results for all these different calculations are presented in Table V and displayed in Fig. 1, along with the experimental data for DWF. For convenience, the results are given in terms of the experimental DWF, B, which is $8\pi^2$ times the theoretical DWF, viz., $2M(\mathbf{q})$ of Eqs. (16)–(18).

The Morse potential DWF with volume dependence shows a nonlinear temperature dependence in the quasiharmonic contribution. Partial cancellation of the

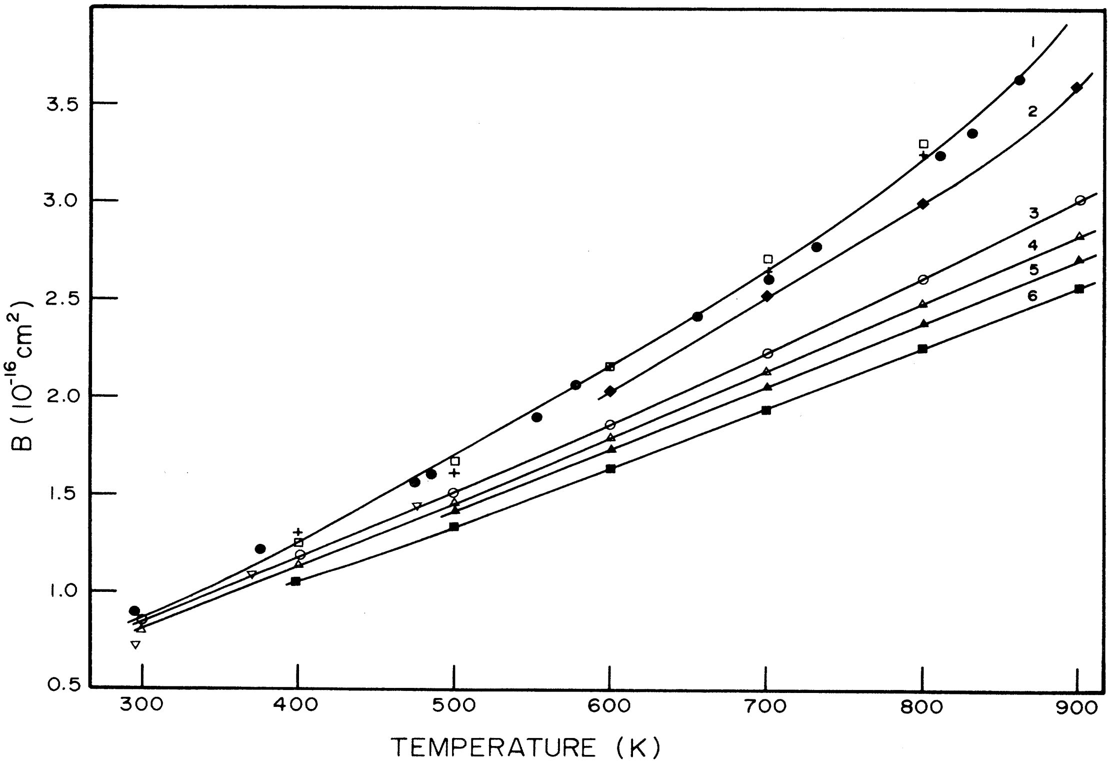

FIG. 1. Temperature dependence of the experimental and calculated Debye-Waller factor (B). Curves 1 and 2 are experimental values: ●, Ref. 20; □, +, Ref. 15; ▽, Ref. 21; ◆, Ref. 17. Curve 3, modified Morse; curve 4, Morse; curve 5, leading-term approximation: LTA; curve 6, Harrison modified point-ion pseudopotential.

cubic and quartic terms reduces the anharmonic contribution to about 50% of the cubic term but leaves a total positive anharmonic contribution. The anharmonic contributions are seen to have a significant volume dependence only above 500 K. The results for the fixed 0 K volume show that most of the volume dependence of DWF lies in the quasiharmonic term.

For the modified Morse potential (Morse 2 in Table V) the cancellation of the quartic and cubic terms is almost complete. At 900 K the sum of these terms is only 10% of the corresponding sum for the Morse potential. The quasiharmonic contribution is larger than for the Morse potential. The results of the PT for these potentials are shown as curves 3 and 4 in Fig. 1.

In the LTA at fixed volume the quasiharmonic portion of the DWF is larger than the Morse PT results with volume dependence. As shown in Table V, the cubic and quartic contributions in LTA show cancellation and sum to a negative value, in contrast to the positive sums for the PT results. The net result, curve 5 for LTA has an upward curvature but is lower than the PT results at all temperatures.

The results for the Harrison pseudopotential exhibit a weak upward curvature, as shown by curve 6 in the high-temperature range. Partial cancellation between the quartic and cubic terms is similar in magnitude to the results for the two Morse potentials and leaves a net positive contribution. The quasiharmonic contribution is smaller than that of any of the other cases examined. A realistic test of this potential would require the redefinition of the parameters of the potential at each volume and temperature.

Experimental measurements of DWF from 300 to 860 K by neutron scattering,[20] from 295 to 800 K by x-ray scattering,[15] and from 300 to 900 K by scattering of recoil-less γ rays,[17] show that the temperature dependence contains linear and quadratic terms in T. A possible cubic dependence on T, discussed in the first two reports[20,15] is not confirmed in the third.[17] These results and some earlier results at the low end of the temperature range[21] are shown in Fig. 1. Above 700 K the DWF determined by scattering of recoil-less γ rays, curve 2, lies below the other results, curve 1. At 850 K the difference is about 7%.

The calculated PT values of DWF for the Morse potentials show a smaller upward curvature than the experimental results. The agreement is good up to 500 K, but the difference between the two sets rises to about 15% at 900 K. The whole set of experimental points can be fitted to the form $B(T)=2.3\times10^{-19}T+2.0\times10^{-22}T^2$ in units of Å^2. Similarly, the calculated points for the modified Morse 2 potential can be fitted to the form $B(T)=2.65\times10^{-19}T+0.77\times10^{-22}T^2$ in units of Å^2. The calculated anharmonic term in T^2 is about 38% of the experimental term while the quasiharmonic terms agree to about 15%.

The experimental results can be reproduced more closely if the parameters of the Morse potentials are altered. However, the new form of the potential will not necessarily be consistent with other properties of the system. The well-depth parameter is one-sixth of the sublimation energy per atom at the 0 K volume. Estimates[22,23] of this energy vary by 30%. The well depth is related to the exponential parameter through the Debye temperature. When new self-consistent values of these two parameters are chosen to match the range of sublimation energies the improvement in the fit to experiment is slight.

VI. CONCLUSION

We have presented a method for an exact calculation of the harmonic and lowest-order (cubic and quartic) anharmonic contributions to the Debye-Waller factor for the NNCF model of a monatomic fcc crystal and applied it to Al. We have also assessed the validity of the leading-term approximation introduced earlier, in such calculations, by Maradudin and Flinn.

Introduction of this approximation gives a negative anharmonic contribution to DWF. The exact calculation gives a positive contribution. A comparison of the theoretical results of DWF with their experimental values in Al shows that the agreement with experimental is good up to 500 K. The theory and experiment differ by 16% at the highest temperature, 900 K. We ascribe this difference to the limited applicability of the Morse potential.

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