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Debye-Waller factor of bcc metals: A comparison of the lattice-dynamics and molecular-dynamics results for Li and Rb

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We present a method for the numerical calculation of the anharmonic contributions to the Debye-Waller factor (DWF) for metals involving long-range interactions. The numerical results of DWF obtained by the above method are compared with those of a molecular-dynamics calculation for a sixth-neighbor-interaction model of Li and Rb. It is shown that an excellent agreement is achieved between the results calculated by the two methods for the same model of the crystal potential. For Li and Rb the anharmonic contribution to DWF of $O(|\vec{q}|^2)$, where $\vec{q}$ is the wave vector, is about 10% of the quasiharmonic contribution at $T \sim T_m$ (T_m is the melting temperature). The two other anharmonic contributions of $O(|\vec{q}|^4)$ to DWF are found to be negligible in Li and Rb even when $T \sim T_m$.

I. INTRODUCTION

As early as 1914 the effect of atomic vibrations on the intensity of x-ray scattering was studied by Debye[1] and nine years later by Waller.[2] Symbolically, if the intensity at temperature T is I and that at 0 K is I_0 then Debye and Waller showed that

$$I = I_0 e^{-2M(\vec{q})} , \tag{1}$$

where for a wave vector $\vec{q}$, $2M(\vec{q})$ is known as the Debye-Waller factor (DWF). $2M(\vec{q})$ is given in terms of the ensemble average of the square of the atomic displacement (u) in the direction of u,

$$2M(\vec{q}) = C\langle u^2 \rangle . \tag{2}$$

In Eq. (2), C is a constant and the angular brackets denote averaging with respect to the harmonic vibration of the crystal. The constant C assumes different values for the various contributions to $2M(\vec{q})$ listed in Sec. III. Explicit forms are indicated in Ref. 3. When the temperature is greater than the Debye temperature (Θ_D), the anharmonic terms in the vibrating crystal cannot be ignored. When this effect is taken into account in the averaging process in Eq. (2), the determination of $2M$ becomes more complex.

Maradudin and Flinn[3] have derived expressions for $2M$ in the high-temperature limit for an anharmonic crystal by retaining the cubic and quartic terms in the Hamiltonian. There are four anharmonic contributions to $2M$. The first two contributions are isotropic and proportional to $|\vec{q}|^2$ whereas the other two are nonisotropic and proportional to $|\vec{q}|^4$. Maradudin and Flinn[3] have also performed numerical calculations of the $|\vec{q}|^2$ and $|\vec{q}|^4$ contributions to $2M$ for a nearest-neighhbor central force (NNCF) model of a fcc crystal. They have employed the leading term approximation in the evaluation of the third- and fourth-rank tensors arising in all the contributions and the Ludwig approximation in the calculation of the two $|\vec{q}|^4$ contributions. As shown by Shukla and Wilk[4] in the anharmonic Helmholtz free-energy calculations, both these approximations are poor. Wolfe and Goodman[5] have also calculated the above mentioned four contributions to $2M$ for a fcc crystal but without making any of the approximations of Maradudin and Flinn.[3] They employed the general-tensor-force model, extending to sixth-neighbor interaction, to compute the phonon frequencies and eigenvectors of the harmonic model but the third- and fourth-rank tensors were evaluated for a NNCF model of a fcc crystal from a Born-Mayer potential. However, it is well known that even in such simple metals as alkalis the forces are of a long-range nature and, as shown by one of us,[6] the nearest-neighbor interaction leads to misleading results in anharmonic calculations of a bcc structure. A search of the existing literature reveals that except for the harmonic calculation of $2M$ by Vaks *et al.*[7] the anharmonic calculations of $2M$ for the bcc structure, such as the alkali metals, have not been carried out in the past.

In this paper we present a method for the numerical calculation of the anharmonic contributions to $2M$ for metals involving long-range interactions and compare our results for a model for Li and Rb with the results of a molecular-dynamics calculation for the same model. As mentioned previously, the methods used by Maradudin and Flinn[3] and Wolfe and Goodman[5] are geared to the anharmonic calculations of $2M$ for the NNCF model of fcc structure.

Our motivation in performing the present calculations of $2M$ also arises for the following two reasons. Firstly, the recent calculation of the high-temperature specific heat of Rb for a sixth-neighbor-model interaction by MacDonald *et al.*[8] showed large discrepancies at high temperatures between the Monte Carlo results and the lowest-order perturbation theory results which included the cubic and quartic terms in the potential energy. The difference in the two results for the specific heat indicates the importance of the higher-order perturbation theory[9] corrections, because, for the same model employed in both calculations, no expansion of the crystal potential is involved in the Monte Carlo calculation. Clearly then it would be of some interest to compare the results for $2M$ obtained from the molecular-dynamics calculation (which again does not require expansion of the potential-energy function) and the lowest-order perturbation theory calculation for the same model of the bcc crystal employed in both the calculations. To the best of our knowledge the molecular-dynamics calculation of $2M$ for the long-range potentials in metals has not been reported so far. Secondly, the recent measurements of the Debye-Waller factor (DWF) or $2M$ in Li by McCarthy *et al.*[10] by incoherent neutron elastic scattering experiments has shown large anharmonic contributions to DWF at all temperatures in their analysis of the data.

The plan of this paper is as follows: Our method of the lattice-dynamics calculation of $2M$ is presented in Sec. II where it is shown that all the contributions (harmonic and anharmonic) of $O(|\vec{q}|^2)$ and $O(|\vec{q}|^4)$ can be evaluated from the knowledge of three different types of second-rank tensors, viz., $S_{\alpha\beta}$, $T_{\alpha\beta}$, and $G_{\alpha\beta}$. This is followed by a description of the molecular-dynamics calculation of $2M$ in Sec. III. The discussion of the numerical results for Li and Rb obtained by the two methods for a sixth-neighbor-interaction model is presented in Sec. IV. Finally, the summary and the conclusions of this work are given in Sec. V.

II. LATTICE-DYNAMICS CALCULATIONS

The lattice-dynamics calculation of the Debye-Waller factor (DWF) or the average square of atomic displacement is essentially a perturbation-type calculation. There are four contributions to the Debye-Waller factor to $O(\lambda^2)$ in the lowest order of perturbation theory, where λ is the perturbation expansion parameter. They arise from the cubic and quartic terms in the Taylor's series expansion of the crystal potential energy. Two of these terms are of $O(T^2)$ and $O(|\vec{q}|^2)$ and the other two are of $O(T^3)$ and $O(|\vec{q}|^4)$, where $\vec{q}$ is the wave vector. In the classical high-temperature limit ($T > \Theta_D$), where Θ_D is the Debye temperature, these contributions were first derived by Maradudin and Flinn.[3] In addition to these four contributions there are two other contributions of $O(|\vec{q}|^2)$ which arise in the harmonic approximation and are due to thermal expansion effects. The last two contributions can be evaluated as one single term calculated in the quasiharmonic approximation.

Representing the quasiharmonic (QH) contribution to DWF by $2M_{\mathrm{QH}}(\vec{q})$ and the four λ^2 contributions by $2M_1(\vec{q})$, $2M_2(\vec{q})$, $2M_3(\vec{q})$, and $2M_4(\vec{q})$, respectively, their mathematical expressions are given by[3]

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

$$2M_1(\vec{q}) = \frac{-(k_B T)^2}{2N^2 M} \sum_{\vec{q}_1 \vec{q}_2} \sum_{j_1 j_2 j_3} \frac{\Phi(\vec{q}_1 j_1, -\vec{q}_1 j_1, \vec{q}_2 j_2, -\vec{q}_2 j_3)[\vec{q}\cdot\vec{\epsilon}(\vec{q}_2 j_2)][\vec{q}\cdot\vec{\epsilon}(\vec{q}_2 j_3)]}{\omega^2(\vec{q}_1 j_1)\omega^2(\vec{q}_2 j_2)\omega^2(\vec{q}_2 j_3)} , \tag{4}$$

$$2M_2(\vec{q})=\frac{(k_BT)^2}{2N^2M}\sum_{\substack{\vec{q}_1\vec{q}_2\vec{q}_3\\ j_1j_2j_3j_4}}\Delta(\vec{q}_1+\vec{q}_2+\vec{q}_3)\Phi(\vec{q}_1j_1,\vec{q}_2j_2,\vec{q}_3j_3)\Phi(-\vec{q}_1j_1,-\vec{q}_2j_2,-\vec{q}_3j_4)$$
$$\times\frac{[\vec{q}\cdot\vec{\epsilon}(\vec{q}_3j_3)][\vec{q}\cdot\vec{\epsilon}(\vec{q}_3j_4)]}{\omega^2(\vec{q}_1j_1)\omega^2(\vec{q}_2j_2)\omega^2(\vec{q}_3j_3)\omega^4(\vec{q}_3j_4)}\,, \tag{5}$$

$$2M_3(\vec{q})=\frac{(k_BT)^3}{12N^3M^2}\sum_{\vec{q}_1\vec{q}_2\vec{q}_3\vec{q}_4}\sum_{j_1j_2j_3j_4}\Delta(\vec{q}_1+\vec{q}_2+\vec{q}_3+\vec{q}_4)\Phi(\vec{q}_1j_1,\vec{q}_2j_2,\vec{q}_3j_3,\vec{q}_4j_4)$$
$$\times\frac{[\vec{q}\cdot\vec{\epsilon}(\vec{q}_1j_1)][\vec{q}\cdot\vec{\epsilon}(\vec{q}_2j_2)][\vec{q}\cdot\vec{\epsilon}(\vec{q}_3j_3)][\vec{q}\cdot\vec{\epsilon}(\vec{q}_4j_4)]}{\omega^2(\vec{q}_1j_1)\omega^2(\vec{q}_2j_2)\omega^2(\vec{q}_3j_3)\omega^2(\vec{q}_4j_4)}\,, \tag{6}$$

$$2M_4(\vec{q})=\frac{-(k_BT)^3}{4N^3M^2}\sum_{\vec{q}_1\vec{q}_2\vec{q}_3}\sum_{j_1j_2j_3}\sum_{\vec{q}_5\vec{q}_6}\sum_{j_5j_6}\Delta(\vec{q}_1+\vec{q}_2+\vec{q}_3)\Delta(-\vec{q}_1+\vec{q}_5+\vec{q}_6)$$
$$\times\Phi(\vec{q}_1j_1,\vec{q}_2j_2,\vec{q}_3j_3)\Phi(-\vec{q}_1j_1,\vec{q}_5j_5,\vec{q}_6j_6)$$
$$\times\frac{[\vec{q}\cdot\vec{\epsilon}(\vec{q}_2j_2)][\vec{q}\cdot\vec{\epsilon}(\vec{q}_3j_3)][\vec{q}\cdot\vec{\epsilon}(\vec{q}_5j_5)][\vec{q}\cdot\vec{\epsilon}(\vec{q}_6j_6)]}{\omega^2(\vec{q}_1j_1)\omega^2(\vec{q}_2j_2)\omega^2(\vec{q}_3j_3)\omega^2(\vec{q}_5j_5)\omega^2(\vec{q}_6j_6)}\,. \tag{7}$$

The various symbols appearing in Eqs. (3)–(7) have the following meaning: M is the atomic mass, k_B is the Boltzmann constant, T is the temperature, N is the number of unit cells in the crystal, and $\omega(\vec{q}j)$ and $\vec{\epsilon}(\vec{q}j)$ are the eigenvalues and eigenvectors, respectively, for the wave vector $\vec{q}$ and branch index j. The delta function $\Delta(\vec{q}_1+\vec{q}_2+\cdots+\vec{q}_n)$ appearing in Eqs. (5)–(7) is unity if $\vec{q}_1+\vec{q}_2+\cdots+\vec{q}_n$ is zero or a vector of the reciprocal lattice ($\vec{\tau}$) and zero otherwise. The Φ functions appearing in Eqs. (4)–(7) are the Fourier transforms of the third- and fourth-order atomic force constants. In general, the Fourier transform of the nth order atomic force constant $\phi_{\alpha\beta\cdots\mu}(\vec{l})$ is defined by the following:

$$\Phi(\vec{q}_1j_1,\vec{q}_2j_2,\ldots,\vec{q}_nj_n)=\frac{1}{2M^{n/2}}\sum_{\vec{l}}{}'\sum_{\alpha\beta\cdots\mu}\phi_{\alpha\beta\cdots\mu}(\vec{l})\epsilon_\alpha(\vec{q}_1j_1)\epsilon_\beta(\vec{q}_2j_2)\cdots\epsilon_\mu(\vec{q}_nj_n)$$
$$\times(1-e^{-i\vec{q}_1\cdot\vec{r}_l})(1-e^{-i\vec{q}_2\cdot\vec{r}_l})\cdots(1-e^{-i\vec{q}_n\cdot\vec{r}_l})\,, \tag{8}$$

where the prime over the direct lattice vector ($\vec{l}$) summation in the previous equation indicates the omission of the origin point.

The numerical calculation of the above five contributions to $2M(\vec{q})$ can be greatly simplified for cubic crystals. For example, when the symmetry operations of a cube are performed on the vector $\vec{q}$, then due to invariance of $2M(\vec{q})$ many terms on the right-hand side of the expressions of $2M_{\text{QH}}(\vec{q})$, $2M_1(\vec{q})$, and $2M_2(\vec{q})$ are equal and the other cross terms are zero. Making use of this property and the orthogonality of eigenvectors we obtain the following simplified expressions for $2M_{\text{QH}}(\vec{q})$, $2M_1(\vec{q})$, and $2M_2(\vec{q})$.

$$2M_{\text{QH}}(\vec{q})=\frac{|\vec{q}\,|^2(k_BT)}{3NM}\sum_{\vec{q}_1j_1}\frac{1}{\omega^2(\vec{q}_1j_1)}\,, \tag{9}$$

$$2M_1(\vec{q})=-|\vec{q}\,|^2\frac{(k_BT)^2}{6N^2M}\sum_{\vec{q}_1\vec{q}_2}\sum_{j_1j_2}\frac{\Phi(\vec{q}_1j_1,-\vec{q}_1j_1,\vec{q}_2j_2,-\vec{q}_2j_2)}{\omega^2(\vec{q}_1j_1)\omega^4(\vec{q}_2j_2)}\,, \tag{10}$$

$$2M_2(\vec{q})=\frac{|\vec{q}|^2(k_BT)^2}{6N^2M}\sum_{\vec{q}_1\vec{q}_2\vec{q}_3}\sum_{j_1j_2j_3}\Delta(\vec{q}_1+\vec{q}_2+\vec{q}_3)\frac{\Phi(\vec{q}_1j_1,\vec{q}_2j_2,\vec{q}_3j_3)\Phi(-\vec{q}_1j_1,-\vec{q}_2j_2,-\vec{q}_3j_3)}{\omega^2(\vec{q}_1j_1)\omega^2(\vec{q}_2j_2)\omega^4(\vec{q}_3j_3)}\ . \tag{11}$$

The expressions for $2M_3(\vec{q})$ and $2M_4(\vec{q})$ are quite lengthy even for cubic crystals. Therefore, we first describe the calculations of $2M_1(\vec{q})$. Substituting the expression for Φ from Eq. (8) into Eq. (4) and expressing the two whole Brillouin-zone (BZ) sums in terms of the two following tensors $S_{\alpha\beta}(\vec{l})$ and $T_{\gamma\delta}(\vec{l})$, introduced previously in anharmonic calculations by Shukla and Wilk,[4] we have for $2M_1(\vec{q})$ the following:

$$2M_1(\vec{q})=\frac{-|\vec{q}|^2(k_BT)^2}{3N^2M^3}\sum_{\vec{l}}\sum_{\alpha\beta\gamma\delta}\phi_{\alpha\beta\gamma\delta}(|\vec{l}|)[S_{\alpha\beta}(0)-S_{\alpha\beta}(\vec{l})][T_{\gamma\delta}(0)-T_{\gamma\delta}(\vec{l})]\ , \tag{12}$$

$$S_{\alpha\beta}(\vec{l})=\sum_{\vec{q}j}\frac{\epsilon_\alpha(\vec{q}j)\epsilon_\beta(\vec{q}j)}{\omega^2(\vec{q}j)}\cos(\vec{q}\cdot\vec{r}_l)\ , \tag{13}$$

$$T_{\alpha\beta}(\vec{l})=\sum_{\vec{q}j}\frac{\epsilon_\alpha(\vec{q}j)\epsilon_\beta(\vec{q}j)}{\omega^4(\vec{q}j)}\cos(\vec{q}\cdot\vec{r}_l)\ . \tag{14}$$

The calculation of $2M_{\rm QH}(\vec{q})$ can also be carried out from the knowledge of the $S_{\alpha\beta}(0)$ tensor obtained from the following expression:

$$2M_{\rm QH}(\vec{q})=\frac{|\vec{q}|^2k_BT}{9NM}[S_{xx}(0)+S_{yy}(0)+S_{zz}(0)]\ . \tag{15}$$

The expression for $2M_3(\vec{q})$ can be reduced in terms of the fourth-rank tensor $H_{\lambda\mu\nu\epsilon}$ with the help of the plane-wave representation of the Δ function, which requires the introduction of another direct lattice sum $(\vec{l})$ in the calculation. Each of the four BZ sums are again expressed in terms of $S_{\alpha\beta}(\vec{l})$ and the final expression for $2M_3(\vec{q})$ is

$$2M_3(\vec{q})=\frac{(k_BT)^3}{24N^4M^4}\sum_{\lambda\mu\nu\epsilon}q_\lambda q_\mu q_\nu q_\epsilon H_{\lambda\mu\nu\epsilon}\ , \tag{16}$$

$$\begin{aligned}H_{\lambda\mu\nu\epsilon}=\sum_{\vec{l}_1}{}'\sum_{\vec{l}}\sum_{\alpha\beta\gamma\delta}\phi_{\alpha\beta\gamma\delta}(|\vec{r}_{l_1}|)&[S_{\alpha\lambda}(\vec{l})-S_{\alpha\lambda}(\vec{l}-\vec{l}_1)][S_{\beta\mu}(\vec{l})-S_{\beta\mu}(\vec{l}-\vec{l}_1)]\\&\times[S_{\gamma\nu}(\vec{l})-S_{\gamma\nu}(\vec{l}-\vec{l}_1)][S_{\delta\epsilon}(\vec{l})-S_{\delta\epsilon}(\vec{l}-\vec{l}_1)]\ .\end{aligned} \tag{17}$$

We note here that for cubic crystals we need to calculate only the following components of $H_{\lambda\mu\nu\epsilon}$: viz., H_{xxxx}, H_{yyyy}, H_{zzzz}; H_{xxyy}, H_{xxzz}, H_{yyzz}; H_{xyxy}, H_{xzxz}, H_{yzyz}.

The calculation of $2M_4(\vec{q})$ is quite tedious. The plane wave representation of the Δ function method, used in the calculation of $2M_3(\vec{q})$, produces very complicated expressions for the numerical work. However, the expression for $2M_4(\vec{q})$ involving the largest number of BZ and branch index summations can be simplified in the following manner. First, we change the sign of $\vec{q}_5$ and $\vec{q}_6$ in Eq. (7) which yields a negative sign due to the property of the Φ function, i.e., $\Phi(-\vec{q}_1j_1,-\vec{q}_5j_5,-\vec{q}_6j_6)=-\Phi(\vec{q}_1j_1,\vec{q}_5j_5,\vec{q}_6j_6)$. Next, we use the even function property of the Δ function, i.e., $\Delta(-\vec{q}_1-\vec{q}_5-\vec{q}_6)=\Delta(\vec{q}_1+\vec{q}_5+\vec{q}_6)$ and the symmetry in the sums $(\vec{q}_2j_2,\vec{q}_3j_3)$ and $(\vec{q}_5j_5,\vec{q}_6j_6)$ to express $2M_4(\vec{q})$ in the following form for computational purposes:

$$2M_4(\vec{q})=\frac{(k_BT)^3}{4N^3M^2}\sum_{\alpha\beta\gamma\delta}q_\alpha q_\beta q_\gamma q_\delta Z_{\alpha\beta\gamma\delta}\ , \tag{18}$$

where

$$Z_{\alpha\beta\gamma\delta}=\sum_{\vec{q}_1j_1}\frac{G_{\alpha\beta}(\vec{q}_1j_1)G_{\gamma\delta}(\vec{q}_1j_1)}{\omega^2(\vec{q}_1j_1)}\ , \tag{19}$$

$$G_{\alpha\beta}(\vec{q}_1 j_1)=\sum_{\vec{q}_2\vec{q}_3}\sum_{j_2 j_3}\Delta(\vec{q}_1+\vec{q}_2+\vec{q}_3)\frac{\Phi(\vec{q}_1 j_1,\vec{q}_2 j_2,\vec{q}_3 j_3)\epsilon_\alpha(\vec{q}_2 j_2)\epsilon_\beta(\vec{q}_3 j_3)}{\omega^2(\vec{q}_2 j_2)\omega^2(\vec{q}_3 j_3)}\,, \tag{20}$$

and a similar expression for $G_{\gamma\delta}(\vec{q}_1 j_1)$. Once again for cubic crystals we only need to calculate Z_{xxxx}, Z_{yyyy}, Z_{zzzz}; Z_{xxyy}, Z_{xxzz}, Z_{yyzz}; Z_{xyxy}, Z_{xzxz}, Z_{yzyz}.

In the numerical calculation of the above contributions to $2M(\vec{q})$ we have employed two methods. The first method required the evaluation of single whole BZ sum in the calculation of the tensors $S_{\alpha\beta}(\vec{l})$ and $T_{\gamma\delta}(\vec{l})$. The whole BZ sum in each case was reduced to the $(\frac{1}{48})$th portion of the irreducible sector by the method presented in Shukla and Wilk.[4] The necessary equations have been presented fully in their paper and there is little point in reproducing them here. Concerning the density of points in the whole BZ, we have used a simple cubic mesh of step length 20 which yields 16 000 points in the whole zone. The procedure in our program was to first calculate and store values of $S_{\alpha\beta}(\vec{l})$ and $T_{\gamma\delta}(\vec{l})$ for a wide range of $\vec{l}$ vectors and then select the required values of the functions as needed in the calculation. This was the method followed especially in the calculation of $2M_3(\vec{q})$. The calculation of $2M_1(\vec{q})$ and $2M_{\mathrm{QH}}(\vec{q})$ was obviously much more straightforward than $2M_3(\vec{q})$.

The calculation of $2M_2(\vec{q})$ and $2M_4(\vec{q})$ is best carried out by the second method (commonly known as the scanning method) the details of which can be obtained from Maradudin and Flinn[3] and Flinn and Maradudin.[11] Some further details concerning the calculation of the Fourier transform of the cubic anharmonic force constant $\Phi(\vec{q}_1 j_1,\vec{q}_2 j_2,\vec{q}_3 j_3)$ can be obtained from Shukla and Taylor.[12] The number of wave vectors or the density of points in the whole BZ required for the convergence of the type of multiple Brillouin zone sums, arising in the calculations of $2M_2(\vec{q})$ and $2M_4(\vec{q})$, have been discussed previously[8,12] in the calculation of the anharmonic contribution to the specific heat (C_v^A) of bcc metals. Since the multiple Brillouin-zone sums arising in $2M_2(\vec{q})$, $2M_4(\vec{q})$, and C_v^A are similar, once again we have used a simple cubic mesh of step length 6 in the calculations of $2M_2(\vec{q})$ and $2M_4(\vec{q})$. This step length yields 432 points in the whole Brillouin zone.

After performing all the relevant direct-lattice and the Brillouin-zone sums in the expressions of the above contributions to $2M$, we find the following simplified expressions for $2M_{\mathrm{QH}}(\vec{q})$, $2M_1(\vec{q})$, $2M_2(\vec{q})$, $2M_3(\vec{q})$, and $2M_4(\vec{q})$:

$$2M_{\mathrm{QH}}=(k_B T)S_{\mathrm{QH}}q^2\,, \tag{21}$$

$$2M_1=(k_B T)^2 S_1 q^2\,, \tag{22}$$

$$2M_2=(k_B T)^2 S_2 q^2\,, \tag{23}$$

$$2M_3=(k_B T)^3[A(q_x^4+q_y^4+q_z^4)+6B(q_x^2q_y^2+q_y^2q_z^2+q_z^2q_x^2)]\,, \tag{24}$$

$$2M_4=(k_B T)^3[C(q_x^4+q_y^4+q_z^4)+(2D+4E)(q_x^2q_y^2+q_y^2q_z^2+q_z^2q_x^2)]\,. \tag{25}$$

The numerical values of the constants S_{QH}, S_1, S_2 appearing in the above q^2 terms and the other constants, viz., A, B, C, D, E, in $2M_3$ and $2M_4$ terms for three different volumes of Rb and one volume of Li are presented in Table I.

The model potentials used in these calculations and in the molecular-dynamics calculation discussed in Sec. III were constructed following the procedure of Price *et al.*[13] The Li potential parameters are $a=3.478$ Å, $r_c=1.40$, $m^*/m=1.30$, $A=0.999$, $r_s=3.236$, and $B=0.258$. The parameters for the Rb potentials are listed in Table 1 of Ref. 8.

III. MOLECULAR-DYNAMICS CALCULATIONS

The classical equations of motion for 250 particles were integrated using the Beeman algorithm which is described by Schofield[14] and by Sangster and Dixon.[15] The force law was obtained using the same effective pair potential employed in the lattice-dynamics calculations. For lithium, distances were measured in units of $\sigma=2.665$ Å, the position of the smallest zero of the pair potential and the energy was scaled by $\epsilon=588.5k_B$, the depth of the well of the pair potential where k_B is Boltzmann's constant. The time unit employed was $\tau=(m\sigma^2/\epsilon)^{1/2}=3.166\times10^{-13}$ s where m is the mass of a lithium atom. The time increment used when integrating the equations of motion was $\Delta t=0.01\tau$. The particles were placed in a cube

TABLE I. Constants used in the calculation of $2M$ for Li and Rb [see Eqs. (21)–(25)]. $S_{\rm QH}$ is in units of 10^{-4} erg^{-1}cm^2; S_1 and S_2 are in units of 10^8 erg^{-2}cm^2, A, B, C, D, and E are units of 10^4 erg^{-3}cm^4.

	Lattice constant (Å)	$S_{\rm QH}$	S_1	S_2	A
Li	3.478	1.1131	−5.8078	7.7178	0.2583
Rb	5.661	3.7294	−16.0902	26.3573	2.7472
	5.700	3.9091	−17.2686	29.1339	3.1483
	5.739	4.1014	−19.6313	32.3254	3.7213
		B	C	D	E
Li	3.478	−0.0114	−0.2426	0.0023	−0.1254
Rb	5.661	−0.1982	−2.9911	0.0661	−1.5073
	5.700	−0.2323	−3.4420	0.0685	−1.7484
	5.739	−0.2604	−3.9791	0.0701	−2.0362

containing $5\times5\times5$ bcc unit cells and periodic boundary conditions were employed to minimize surface effects. During the course of each computation, the kinetic energy per particle and the Fourier coefficients for the density with wave vectors pointing in the [100], [110], and [111] directions of the cube were calculated and stored for later processing.

The influence of the initial bcc configuration was eliminated by carefully aging the system for several thousand time steps before collecting data. The stability of the results was checked by comparing averages made during sequential computations (the final configuration for one computation was the initial configuration for the following computation) and only when temperature stability was achieved did we assume that the influence of the initial conditions had been eliminated. The fluctuations in the kinetic energy were used as an indicator of the stationarity of the system in the following way. The microcanonical ensemble expression relating the kinetic energy fluctuations of N particles to C_v, the specific heat at constant volume, is[16,17]

$$\frac{C_v}{k_B}=\frac{3}{2}\left[1-\tfrac{3}{2}N\frac{\langle(\Delta K)^2\rangle}{\langle K\rangle^2}\right]^{-1} . \tag{26}$$

Here, K is the kinetic energy per particle. $\langle(\Delta K)^2\rangle=\langle K^2\rangle-\langle K\rangle^2$ and the angular brackets indicate a microcanonical average evaluated as

$$\langle f\rangle=\frac{1}{T}\int_0^T dt\, f(t) . \tag{27}$$

The estimate for the specific heat obtained using Eq. (26) is fairly sensitive to temperature drifts associated with incomplete equilibrium in a constant energy system. We required that the estimate for C_v/k_B obtained using Eq. (26) be in the range of 3–4 before the results were accepted as stationary. We performed calculations for four states over the temperature interval $189\ {\rm K}\le T\le 470$ K. We note that the variation of the system energy with temperature over this interval, as shown in Fig. 1 is $C_v/k_B=3.1\pm0.3$. The uncertainty in the temperature was determined from the rms fluctuation in the kinetic energy.

The structure factor for wave vector Q is just the mean-square density fluctuation of wave vector Q; that is,

$$S(Q)=\langle n_Q n_{-Q}\rangle , \tag{28}$$

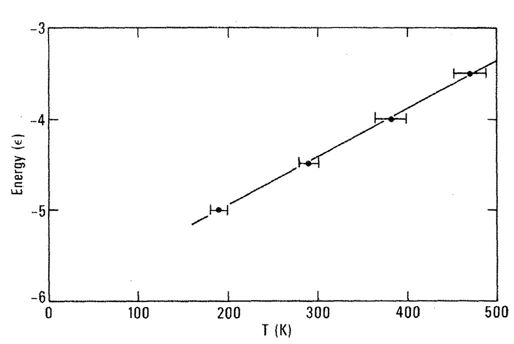

FIG. 1. Molecular-dynamics results for the energy-temperature variation for Li at constant volume. The energy is in units of $\epsilon=588.5k_B$ where k_B is Boltzmann's constant. The uncertainties in the temperature are determined from the fluctuations in the kinetic energy. The straight line corresponds to a specific heat at constant volume $C_v/k_B=3.1\pm0.3$.

where

$$n_Q = \frac{1}{\sqrt{N}} \sum_j \exp(i\vec{Q}\cdot\vec{r}_j) \tag{29}$$

is the Qth Fourier coefficient of the density. If $\vec{Q}=\vec{G}$, a reciprocal-lattice vector, then

$$S(\vec{G}) = N\exp[-2M(\vec{G})] \,, \tag{30}$$

where $\exp[-2M(\vec{G})]$ is the Debye-Waller factor. The wave-vector dependence of $2M$ obtained from our molecular-dynamics results were examined by plotting $2M/Q^2$ vs Q^2. Our results may be represented as

$$\frac{2M}{Q^2} = \tfrac{1}{3}\langle(\Delta r)^2\rangle - FQ^2 \,. \tag{31}$$

The $\langle(\Delta r)^2\rangle$ and F values obtained from this analysis are listed in Table II for the four temperatures simulated. Each computation was 2000 time-steps long. Fourier coefficients for the [110], [200], [220], and [222] reciprocal lattice vectors were generated for each step. In order to improve statistics, the average in Eq. (28) was made over three equivalent, orthogonal directions for each wave vector. The quoted uncertainties for F were obtained by comparing results from different runs. The values of $\langle(\Delta r)^2\rangle$ were not sensitive to these variations.

The molecular-dynamics results for rubidium were taken from another study of rubidium (unpublished work)[18] using a potential with $\sigma=4.48$ Å and $\epsilon=393k_B$. The methods employed were the same as those used in the lithium calculations except that only the (200) Bragg peaks were obtained. For this reason, the F coefficient of Eq. (31) cannot be obtained from these calculations. The $\langle(\Delta r)^2\rangle$ values listed in Table II are for $n\sigma^3=0.95$ ($a=5.739$ Å) where n is the number density and $\sigma=4.48$ Å.

IV. DISCUSSION

The numerical results reported in this paper were obtained using the potential of Price *et al.*[13] truncated at the sixth-neighbor distance. A summary of the lattice-dynamics and molecular-dynamics results for Li and Rb is contained in Table III.

For the temperatures considered, the two methods are in good agreement although the results begin to separate at the highest temperatures. This is consistent with the specific-heat results for Rb obtained previously[8] using the Monte Carlo method and lowest-order perturbation theory. In that calculation, significant differences in C_v were found for $T > 340$ K but only small differences were found for $T < 340$ K. The results of these two calculations indicate that lattice dynamics provides estimates of thermal properties of Rb which are consistent with simulation results for temperatures up to the melting point but which underestimate thermal values at higher temperatures.

From the results presented in Table III it is apparent that the anharmonic portion of the q^2 contribution to the Debye-Waller factor is of the order of 10% of the quasiharmonic contribution at the melting temperature. This is true for all three volumes for Rb and for the one volume for Li for which we have carried out our calculations. Using lattice dynamics, the q^4 contribution was found to be unimportant in all cases. The largest contribution to $2M$ comes from the quasiharmonic portion of the q^2 term. On the other hand, the molecular-dynamics results indicate that a q^4 term is needed to adequately represent $2M$ for Li at higher temperatures. This indicates that the lattice-dynamics calculations underestimate the magnitude of the q^4 anharmonic contribution.

The density and temperature variation of $\langle(\Delta r)^2\rangle$ for Rb, as predicted by lattice dynamics, is

TABLE II. Molecular-dynamics results for the Debye-Waller factors of Li and Rb.

	Li			Rb
T (K)	$\langle(\Delta r)^2\rangle/(\sigma^2)$	$F/(\sigma^4)$	T (K)	$\langle(\Delta r)^2\rangle/(\sigma^2)$
189±8	0.0130	0.000 04±0.000 04	65±2	0.005 87
290±11	0.0190	0.000 08±0.000 03	158±4	0.0136
382±15	0.0272	0.000 18±0.000 02	218±6	0.0195
470±18	0.0367	0.000 31±0.000 05	279±8	0.0267
			340±10	0.0345

TABLE III. Summary of $\langle u^2 \rangle$ results for Li and Rb using lattice dynamics and molecular dynamics. $\langle u^2 \rangle$ in units of 10^{-16} cm^2. Quasihamonic (QH) and anharmonic contributions are listed separately. The q^4 contribution to AH is negligible.

T (K)	QH	AH	Total	Molecular-dynamics
		Li		
189	0.029 045 65	0.001 300 55	0.030 346 21	0.0308
290	0.044 567 4	0.003 062 0	0.047 629 38	0.0450
382	0.058 706 0	0.005 312 9	0.064 018 94	0.0644
470	0.072 229 9	0.008 042 6	0.080 272 62	0.0869
		Rb		
65	0.036 807	0.001 022	0.037 829	0.0393
158	0.089 469	0.006 04	0.095 510	0.0910
218	0.123 445	0.011 499 8	0.134 945	0.130
279	0.157 987	0.018 836	0.176 823	0.179
340	0.192 529	0.027 973	0.220 502	0.231

presented in Table IV. As expected, $\langle (\Delta r)^2 \rangle$ increases with increasing temperature and decreases with increasing density. Based on the above discussion, we expect that a molecular-dynamics study of $2M$ for the two higher densities would only confirm these results.

V. SUMMARY AND CONCLUSIONS

We have examined the influence of anharmonicity on the Debye-Waller factor of the alkali Li and Rb. This was done by comparing the results of lattice-dynamics calculations with those of molecular-dynamics simulations for the same model potential and thermodynamic states. Several interesting observations result from this comparison.

The first observation is that the lattice-dynamics values of the Debye-Waller factor are in good agreement with the molecular-dynamics values for temperatures up to the melting temperatures of both Li and Rb. At higher temperatures, there is an indication that the anharmonic terms are not adequately described by the q^4 terms appearing in Eqs. (24) and (25). This suggests that the domain of validity of the lattice-dynamical theory included most of the solid phase for the alkali metals.

Experimental results for the Debye-Waller factor of Li were reported in Ref. 10 in terms of the coefficients of Eq. (31). A comparison of the experimental results found in Fig. 7 of Ref. 10 with the corresponding molecular-dynamics results listed in Table II reveals that the experimental values of the q^2 coefficient are approximately twice the magnitude of the molecular-dynamics q^2 coefficients while at 290 K, the experimental value of the q^4 coefficient is smaller than the molecular-dynamics by at least a factor of 4. Since anharmonic effects contribute to both the q^2 and q^4 coefficients, as indicated by Eqs. (22)–(25), it is not possible to state how the potential used in our calculations would have to be modified in order to account for the experimental results. We can assert that the lattice-dynamical theory presented here would provide a good way to test other potentials for Li.

Finally, we observe that the quasiharmonic ap-

TABLE IV. Density and temperature dependence of $\langle (\Delta r)^2 \rangle / \sigma^2$ for Rb as determined by lattice dynamics.

T (K) $n\sigma^3$	0.99	0.97	0.95
65	0.005 13	0.005 39	0.005 65
158	0.012 89	0.013 59	0.014 28
218	0.018 17	0.019 19	0.020 17
279	0.023 75	0.025 14	0.026 43
340	0.029 55	0.031 34	0.032 96

proximation, in which the $\omega(\vec{q}j)$'s are determined for the volume of interest rather than for the $T=0$ K equilibrium volume provides a good starting point for lattice-dynamical calculations. For the Debye-Waller factor for the alkali metals, it provides about 90% of the answer. The procedures set forth in Sec. II for evaluating the anharmonic contribution to the Debye-Waller factor provide the remaining 10%.

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