it possible to study the magnetoplasma resonance in a much broader class of metals than has been previously studied. The work shows the potential and the limitations of this probeless technique for measuring the Hall coefficient and magnetoresistivity.

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# Anharmonic Contributions to the Debye-Waller Factor

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Cubic- and quartic-anharmonic contributions to the Debye-Waller factor of a Bravais lattice have been obtained in the classical limit. The contributions are of two types: One is proportional to the square of the absolute temperature, and the other is proportional to the cube of the temperature. This is in contrast to the linear dependence on the absolute temperature of the Debye-Waller factor in the harmonic approximation. The first type of anharmonic contributions represents just the anharmonic corrections to the mean square amplitude of vibration of an atom, while the second type of term is related to the thermal average of the fourth power of an atomic displacement. These results have the consequence that with the anharmonic contributions included, the Debye-Waller factor for a cubic crystal is no longer isotropic in the components of the scattering vector, although it possesses cubic symmetry. The anharmonic contributions are evaluated numerically for a fcc crystal with nearest-neighbor, central-force interactions. The anharmonic contributions to the intensity of x rays scattered by one-phonon processes are discussed briefly.

## I. INTRODUCTION

THE intensity of x rays scattered by the thermal vibrations of a monatomic Bravais lattice is proportional to the sum[1]

$$I=\sum_{ll'} \exp\{i\boldsymbol{\kappa}\cdot[\mathbf{x}(l)-\mathbf{x}(l')]+i\boldsymbol{\kappa}\cdot[\mathbf{u}(l)-\mathbf{u}(l')]\}, \quad (1.1)$$

where $\mathbf{x}(l)$ is the position vector of the $l$th unit cell in the crystal and $\mathbf{u}(l)$ is the displacement of the $l$th atom from its equilibrium position. The vector $\boldsymbol{\kappa}$ is given by

$$\boldsymbol{\kappa}=(2\pi/\lambda)(\mathbf{s}-\mathbf{s}_0), \quad (1.2)$$

where $\mathbf{s}_0$ and $\mathbf{s}$ are unit vectors in the directions of the normals to the wave fronts of the incoming and scattered x rays, respectively, while $\lambda$ is the wavelength of the x rays.

The displacements $\{\mathbf{u}(l)\}$ are time dependent so that the expression (1.1) gives the instantaneous intensity. The observed intensity can be regarded as the average of (1.1) over a time long compared with the period of the atomic vibrations but short on a macroscopic scale. However, it is usually easier in statistical mechanical problems to replace time averages by ensemble averages, and this is the procedure we follow here. Thus, to obtain the expression for the observed scattered intensity we must evaluate the thermal average,

$$\langle\exp\{i\boldsymbol{\kappa}\cdot[\mathbf{u}(l)-\mathbf{u}(l')]\}\rangle =\frac{\int \exp\{-\beta H+i\boldsymbol{\kappa}\cdot[\mathbf{u}(l)-\mathbf{u}(l')]\}d\Omega}{\int \exp(-\beta H)d\Omega}, \quad (1.3)$$

where $H$ is the lattice Hamiltonian and $d\Omega$ is the appropriate volume element of phase space.

The expression given by Eq. (1.3) represents the thermal average calculated in the classical or "high-temperature" limit. We have chosen to work in this limit because the effects we are studying in this paper are expected to be largest at high temperatures.

In the case that the lattice Hamiltonian is that appropriate to a harmonic crystal, in which case we denote it by $H_0$, the average given by Eq. (1.3) was evaluated first in 1914 by Debye,[2] whose analysis was subsequently corrected by Faxén[3] and by Waller.[4] However, no crystal is truly harmonic and the effects of anharmonic terms in the lattice Hamiltonian on all thermal properties of solids become more important as

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[1] R. W. James, *The Optical Principles of the Diffraction of X-Rays* (G. Bell and Sons, London, 1954), Chap. V. To obtain the intensity in electron units the sum $I$ must be multiplied by $|f_0|^2$, where $f_0$ is the atomic scattering factor.

[2] P. Debye, Ann. Physik **43**, 49 (1914).

[3] H. Faxén, Ann. Physik **54**, 615 (1918).

[4] I. Waller, Z. Physik **17**, 398 (1923).

the temperature increases. In 1927, Waller[5] investigated the effect of cubic anharmonic terms on the average in Eq. (1.3). His results were applied to a rather nonphysical model of a crystal and hence can only be regarded as suggestive. In addition, for Bravais lattices it is known that the quartic anharmonic terms give contributions which are of the same order of magnitude as the cubic term, so that their effects should not be ignored.

In this paper we calculate the leading anharmonic contributions to the thermal average in Eq. (1.3). In particular, we are interested in those terms in the average which are independent of both $l$ and $l'$, the zero-phonon terms in quantum-mechanical language, since these comprise the so-called Debye-Waller factor, which gives the effect of the thermal motion on the intensity of the Bragg reflections.

When the greatest portion of this paper had been completed, we learned of a paper on the same subject by Hahn and Ludwig.[6] The emphasis in their paper, however, is on the intensity of the x rays scattered by one-phonon processes, while we have considered primarily the Debye-Waller factor. Also, the methods employed to calculate the scattered x-ray intensity differ somewhat between the two papers, and we have carried out a numerical evaluation of the anharmonic contributions to the Debye-Waller factor for a simple model of a three-dimensional crystal in this paper. We are grateful to Dr. Hahn and Dr. Ludwig for bringing their work to our attention.

As an introduction to the somewhat more complex anharmonic calculations to be carried out in succeeding sections we present in the remainder of this section a brief calculation of the thermal average (1.3) in the harmonic approximation. In this case it is convenient to expand the displacement component $u_x(l)$ in terms of (complex) normal coordinates

$$u_x(l)=\frac{1}{(NM)^{1/2}}\sum_{\mathbf{k}j} e_x(\mathbf{k}j)Q(\mathbf{k}j)e^{2\pi i\mathbf{k}\cdot\mathbf{x}(l)}. \tag{1.4}$$

In this equation $M$ is the atomic mass, $e_x(\mathbf{k}j)$ is the $x$ component of an eigenvector of the dynamical matrix, $j$ labels the branches of the frequency spectrum, and the allowed values of the wave vector $\mathbf{k}$ are uniformly distributed throughout a unit cell of the reciprocal lattice. The expression $\boldsymbol{\kappa}\cdot[\mathbf{u}(l)-\mathbf{u}(l')]$ in terms of the normal coordinates becomes

$$\begin{aligned}\boldsymbol{\kappa}\cdot[\mathbf{u}(l)-\mathbf{u}(l')]&\\ &=\frac{1}{(NM)^{1/2}}\sum_{\mathbf{k}j}[\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}j)](e^{2\pi i\mathbf{k}\cdot\mathbf{x}(l)}-e^{2\pi i\mathbf{k}\cdot\mathbf{x}(l')})Q(\mathbf{k}j)\\ &=\sum_{\mathbf{k}j}C(\mathbf{k}j)Q(\mathbf{k}j).\end{aligned} \tag{1.5}$$

This equation defines the coefficient $C(\mathbf{k}j)$. Although it is not explicitly expressed, it should be kept in mind that it is a function of both $l$ and $l'$.

The Hamiltonian in the harmonic approximation becomes

$$H_0=\tfrac{1}{2}\sum_{\mathbf{k}j}[\dot{Q}(\mathbf{k}j)\dot{Q}(-\mathbf{k}j)+\omega^2(\mathbf{k}j)Q(\mathbf{k}j)Q(-\mathbf{k}j)], \tag{1.6}$$

where $\omega(\mathbf{k}j)$ is the frequency of the $(\mathbf{k}j)$ normal mode.

Ignoring the kinetic energy terms in the Hamiltonian, since they cancel between the numerator and denominator in Eq. (1.3), we can write the required thermal average as

$$\langle\exp\{i\boldsymbol{\kappa}\cdot[\mathbf{u}(l)-\mathbf{u}(l')]\}\rangle_0=\frac{\displaystyle\int\exp[-\tfrac{1}{2}\beta\sum_{\mathbf{k}j}\omega^2(\mathbf{k}j)Q(\mathbf{k}j)Q(-\mathbf{k}j)+i\sum_{\mathbf{k}j}C(\mathbf{k}j)Q(\mathbf{k}j)]d\Omega}{\displaystyle\int\exp[-\tfrac{1}{2}\beta\sum_{\mathbf{k}j}\omega^2(\mathbf{k}j)Q(\mathbf{k}j)Q(-\mathbf{k}j)]d\Omega}, \tag{1.7}$$

where the subscript 0 indicates that the thermal average is being evaluated in the harmonic approximation. We now manipulate the expression in the exponent of the integrand in the numerator. We express it as

$$\begin{aligned}E=&-\tfrac{1}{2}\beta\sum_{\mathbf{k}j}\omega^2(\mathbf{k}j)Q(\mathbf{k}j)Q(-\mathbf{k}j)\\ &+\tfrac{1}{2}i\sum_{\mathbf{k}j}[C(\mathbf{k}j)Q(\mathbf{k}j)+C(-\mathbf{k}j)Q(-\mathbf{k}j)],\end{aligned} \tag{1.8}$$

where we have replaced $\mathbf{k}$ by $-\mathbf{k}$ as the summation variable in the last term of this expression. We now factor the sum over $\mathbf{k}$ and $j$ as follows:

$$\begin{aligned}E=&-\tfrac{1}{2}\beta\sum_{\mathbf{k}j}\omega^2(\mathbf{k}j)\Big\{Q(\mathbf{k}j)Q(-\mathbf{k}j)\\ &-\frac{i}{\beta\omega^2(\mathbf{k}j)}[C(\mathbf{k}j)Q(\mathbf{k}j)+C(-\mathbf{k}j)Q(-\mathbf{k}j)]\Big\}\\ =&-\tfrac{1}{2}\beta\sum\omega^2(\mathbf{k}j)\bigg\{\bigg[Q(\mathbf{k}j)-\frac{i}{\beta\omega^2(kj)}C(-\mathbf{k}j)\bigg]\\ &\times\bigg[Q(-\mathbf{k}j)-\frac{i}{\beta\omega^2(\mathbf{k}j)}C(\mathbf{k}j)\bigg]\\ &+\frac{1}{\beta^2\omega^4(\mathbf{k}j)}C(\mathbf{k}j)C(-\mathbf{k}j)\bigg\}.\end{aligned} \tag{1.9}$$

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[5] I. Waller, Ann. Physik **83**, 153 (1927).

[6] H. Hahn and W. Ludwig, Z. Physik **161**, 404 (1961).

We next introduce new variables $\{P(\mathbf{k}j)\}$ by

$$P(\mathbf{k}j)=Q(\mathbf{k}j)-\frac{i}{\beta\omega^2(\mathbf{k}j)}C(-\mathbf{k}j). \tag{1.10}$$

(This transformation is due to Waller.[5]) In terms of these variables we can write the exponent as

$$E=-\frac{1}{2\beta}\sum_{\mathbf{k}j}\frac{C(\mathbf{k}j)C(-\mathbf{k}j)}{\omega^2(\mathbf{k}j)}-\tfrac{1}{2}\beta\sum_{\mathbf{k}j}\omega^2(\mathbf{k}j)P(\mathbf{k}j)P(-\mathbf{k}j), \tag{1.11}$$

so that the thermal average becomes

$$\langle\exp\{i\boldsymbol{\kappa}\cdot[\mathbf{u}(l)-\mathbf{u}(l')]\}\rangle_0 =\exp\left[-\tfrac{1}{2}kT\sum_{\mathbf{k}j}\frac{C(\mathbf{k}j)C(-\mathbf{k}j)}{\omega^2(\mathbf{k}j)}\right] \times\frac{\int\exp[-\tfrac{1}{2}\beta\sum_{\mathbf{k}j}\omega^2(\mathbf{k}j)P(\mathbf{k}j)P(-\mathbf{k}j)]d\Omega(P)}{\int\exp[-\tfrac{1}{2}\beta\sum_{\mathbf{k}j}\omega^2(\mathbf{k}j)Q(\mathbf{k}j)Q(-\mathbf{k}j)]d\Omega}. \tag{1.12}$$

In this expression $d\Omega(P)$ is the volume element in the "phase space" of the variables $\{P(\mathbf{k}j)\}$.

Because our change of variables is a linear translation of the old normal coordinates, the Jacobian of the transformation is unity. Furthermore, the fact that our "integrations" in the numerator are carried out along paths displaced from the old ones by $-i/\beta\omega^2(\mathbf{k}j)$ does not alter the value of the integral, according to Cauchy's theorem. Thus, the integrals in numerator and denominator cancel and we are left with

$$\langle\exp\{i\boldsymbol{\kappa}\cdot[\mathbf{u}(l)-\mathbf{u}(l')]\}\rangle_0 =\exp\left\{-\frac{kT}{NM}\sum_{\mathbf{k}j}\frac{[\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}j)]^2}{\omega^2(\mathbf{k}j)}\right\} \times\exp\left\{\frac{kT}{NM}\sum_{\mathbf{k}j}\frac{[\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}j)]^2}{\omega^2(\mathbf{k}j)}\cos\{2\pi\mathbf{k}\cdot[\mathbf{x}(l)-\mathbf{x}(l')]\}\right\}, \tag{1.13}$$

where we have used the explicit expression for $C(\mathbf{k}j)$. The first factor is the Debye-Waller factor with which we are concerned in what follows. It is easily shown from Eq. (1.4) that

$$\langle[\boldsymbol{\kappa}\cdot\mathbf{u}(l)]^2\rangle_0=\frac{kT}{NM}\sum_{\mathbf{k}j}\frac{[\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}j)]^2}{\omega^2(\mathbf{k}j)}, \tag{1.14}$$

so that the Debye-Waller factor can be expressed alternatively as

$$\exp\{-\langle[\boldsymbol{\kappa}\cdot\mathbf{u}(l)]^2\rangle_0\}=\exp(-2M_0) \tag{1.15}$$

for a harmonic lattice.

In the special case of a cubic Bravais lattice, with which we are primarily concerned in what follows, the expression for $2M_0$ simplifies greatly. Expanding the square, $[\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}j)]^2$, in the numerator, we find that all cross terms between the components of $\mathbf{e}(\mathbf{k}j)$ sum to zero since the product $e_x(\mathbf{k}j)e_y(\mathbf{k}j)$ transforms as $k_xk_y$ while $\omega^2(\mathbf{k}j)$ has cubic symmetry. Furthermore, due to cubic symmetry,

$$\sum_{\mathbf{k}j}\frac{e_x^2(\mathbf{k}j)}{\omega^2(\mathbf{k}j)}=\sum_{\mathbf{k}j}\frac{e_y^2(\mathbf{k}j)}{\omega^2(\mathbf{k}j)}=\sum_{\mathbf{k}j}\frac{e_z^2(\mathbf{k}j)}{\omega^2(\mathbf{k}j)}=\tfrac{1}{3}\sum_{\mathbf{k}j}\frac{1}{\omega^2(\mathbf{k}j)}, \tag{1.16}$$

where we have used the normalization of the eigenvectors. We thus obtain for this case that

$$2M_0=\frac{kT}{3NM}\kappa^2\sum_{\mathbf{k}j}\frac{1}{\omega^2(\mathbf{k}j)}. \tag{1.17}$$

We now turn to the calculation of the cubic and quartic anharmonic contributions to the exponent $2M$.

## II. THE ANHARMONIC CONTRIBUTIONS TO THE DEBYE-WALLER FACTOR

The anharmonic terms in the lattice Hamiltonian that we retain are the cubic and quartic terms which, expressed in terms of the $\{Q(\mathbf{k}j)\}$, become

$$\begin{aligned}H_A={}&\frac{1}{6\sqrt{N}}\sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}\sum_{j_1j_2j_3}\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)\Phi(\mathbf{k}_1j_1;\mathbf{k}_2j_2;\mathbf{k}_3j_3)Q(\mathbf{k}_1j_1)Q(\mathbf{k}_2j_2)Q(\mathbf{k}_3j_3)\\&+\frac{1}{24N}\sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3\mathbf{k}_4}\sum_{j_1j_2j_3j_4}\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4)\Phi(\mathbf{k}_1j_1;\mathbf{k}_2j_2;\mathbf{k}_3j_3;\mathbf{k}_4j_4)Q(\mathbf{k}_1j_1)Q(\mathbf{k}_2j_2)Q(\mathbf{k}_3j_3)Q(\mathbf{k}_4j_4)+\cdots,\end{aligned} \tag{2.1}$$

where the $\Phi$ coefficients are essentially the Fourier transforms of the cubic and quartic atomic force constants, and are given explicitly by Born and Huang.[7] The function $\Delta(\mathbf{k})$ equals unity if $\mathbf{k}$ is zero or a translation vector of the reciprocal lattice and vanishes otherwise. We write Eq. (2.1) symbolically as

$$H_A=\lambda V_3+\lambda^2V_4, \tag{2.2}$$

where $\lambda$ is an order parameter which can be equated to unity at the end of the calculation.

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[7] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, Oxford, 1954), Sec. 39.

The formal expression for the thermal average of $\exp\{i\boldsymbol{\kappa}\cdot[\mathbf{u}(l)-\mathbf{u}(l')]\}$ becomes

$$\langle\exp\{i\boldsymbol{\kappa}\cdot[\mathbf{u}(l)-\mathbf{u}(l')]\}\rangle=\frac{\int\exp\{-\beta H_0-\beta H_A+i\boldsymbol{\kappa}\cdot[\mathbf{u}(l)-\mathbf{u}(l')]\}d\Omega}{\int\exp(-\beta H_0-\beta H_A)d\Omega}. \tag{2.3}$$

If we now make the change of variables given by Eq. (1.10), where we now put

$$A(\mathbf{k}j)=\frac{C(-\mathbf{k}j)}{\beta\omega^2(\mathbf{k}j)}=\frac{1}{(NM)^{1/2}}\frac{[\boldsymbol{\kappa}\cdot\mathbf{e}(-\mathbf{k}j)]}{\beta\omega^2(\mathbf{k}j)}(e^{-2\pi i\mathbf{k}\cdot\mathbf{x}(l)}-e^{-2\pi i\mathbf{k}\cdot\mathbf{x}(l')}), \tag{2.4}$$

in light of the calculations of the preceding section we obtain

$$\langle\exp\{i\boldsymbol{\kappa}\cdot[\mathbf{u}(l)-\mathbf{u}(l')]\}\rangle=\langle\exp\{i\boldsymbol{\kappa}\cdot[\mathbf{u}(l)-\mathbf{u}(l')]\}\rangle_0\int\exp(-\beta H_0-\beta H_A-\beta\Delta H_A')d\Omega(P)\bigg/\int\exp(-\beta H_0-\beta H_A)d\Omega. \tag{2.5}$$

In this expression, as before, the subscript 0 denotes the thermal average in the harmonic approximation. The perturbation Hamiltonian $\Delta H_A'$ is given explicitly by

$$\begin{aligned}\Delta H_A'=&\frac{1}{6\sqrt{N}}\sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}\sum_{j_1j_2j_3}\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)\Phi(\mathbf{k}_1j_1;\mathbf{k}_2j_2;\mathbf{k}_3j_3)[3iP(\mathbf{k}_1j_1)P(\mathbf{k}_2j_2)A(\mathbf{k}_3j_3)\\&-3P(\mathbf{k}_1j_1)A(\mathbf{k}_2j_2)A(\mathbf{k}_3j_3)-iA(\mathbf{k}_1j_1)A(\mathbf{k}_2j_2)A(\mathbf{k}_3j_3)]+\frac{1}{24N}\sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3\mathbf{k}_4}\sum_{j_1j_2j_3j_4}\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4)\\&\times\Phi(\mathbf{k}_1j_1;\mathbf{k}_2j_2;\mathbf{k}_3j_3;\mathbf{k}_4j_4)[4iP(\mathbf{k}_1j_1)P(\mathbf{k}_2j_2)P(\mathbf{k}_3j_3)A(\mathbf{k}_4j_4)-6P(\mathbf{k}_1j_1)P(\mathbf{k}_2j_2)A(\mathbf{k}_3j_3)A(\mathbf{k}_4j_4)\\&-4iP(\mathbf{k}_1j_1)A(\mathbf{k}_2j_2)A(\mathbf{k}_3j_3)A(\mathbf{k}_4j_4)+A(\mathbf{k}_1j_1)A(\mathbf{k}_2j_2)A(\mathbf{k}_3j_3)A(\mathbf{k}_4j_4)],\end{aligned} \tag{2.6}$$

where we have used the fact that the $\Phi$ functions are completely symmetric in the interchange of any pair of $(\mathbf{k}j)$'s. In this expression, the terms which contain the $\{P(\mathbf{k}j)\}$ we denote by $\Delta H_A$, while the two terms independent of the $\{P(\mathbf{k}j)\}$ we denote by the constant $A$. Thus we have that

$$\Delta H_A'=\Delta H_A+A, \tag{2.7}$$

and Eq. (2.5) becomes

$$\langle\exp\{i\boldsymbol{\kappa}\cdot[\mathbf{u}(l)-\mathbf{u}(l')]\}\rangle=\langle\exp\{i\boldsymbol{\kappa}\cdot[\mathbf{u}(l)-\mathbf{u}(l')]\}\rangle_0\times\exp(-\beta A)\frac{\int\exp(-\beta H_0-\beta H_A-\beta\Delta H_A)d\Omega(P)}{\int\exp(-\beta H_0-\beta H_A)d\Omega}. \tag{2.8}$$

Although the integrands appearing in the numerator and denominator of this expression are functions of different variables and the integrations are carried out over different paths, in what follows we can ignore these differences and consider the $P$ variables as just the same as the $Q$ variables. This follows from the relations

$$Z_0^{-1}\int\exp(-\beta H_0)P(\mathbf{k}j)d\Omega(P)=0,$$

$$Z_0^{-1}\int\exp(-\beta H_0)P(\mathbf{k}j)P(\mathbf{k}'j')d\Omega(P)=\Delta(\mathbf{k}+\mathbf{k}')\delta_{jj'}\frac{kT}{\omega^2(\mathbf{k}j)},\ \text{etc.}, \tag{2.9}$$

where $Z_0$ is the partition function of the crystal in the harmonic approximation. These relations are readily established by transforming the variables back to the $\{Q(\mathbf{k}j)\}$.

The integral in the denominator of Eq. (2.8) is just the partition function for an anharmonic crystal whose Hamiltonian is $H_0+H_A$. This, by definition, can be written as

$$\int\exp(-\beta H_0-\beta H_A)d\Omega=e^{-\beta F}, \tag{2.10}$$

where $F$ is the crystal's Helmholtz free energy. The integral in the numerator can be regarded formally as the partition function of an anharmonic crystal whose Hamiltonian is $H_0+H_A+\Delta H_A$. By definition, this can be written as

$$\int \exp(-\beta H_0-\beta H_A-\beta\Delta H_A)d\Omega(P)=e^{-\beta(F+\Delta F)}, \tag{2.11}$$

where $F+\Delta F$ is the Helmholtz free energy of the crystal. $\Delta F$ is the contribution to the Helmholtz free energy from those terms which involve $\Delta H_A$ at least once. Combining Eqs. (2.8), (2.10), and (2.11) we obtain the formal result that

$$\begin{aligned}&\langle\exp\{i\boldsymbol{\kappa}\cdot[\mathbf{u}(l)-\mathbf{u}(l')]\}\rangle\\ &\qquad=\langle\exp\{i\boldsymbol{\kappa}\cdot[\mathbf{u}(l)-\mathbf{u}(l')]\}\rangle_0 e^{-\beta A-\beta\Delta F}.\end{aligned} \tag{2.12}$$

Sophisticated techniques for calculating the Helmholtz free energy of an anharmonic crystal have recently been developed by Van Hove.[8] However, since we have retained only terms up to $O(\lambda^2)$ in our anharmonic Hamiltonian, we are justified in keeping only terms up to $O(\lambda^2)$ in $\Delta F$, and to this approximation a simpler treatment suffices. We begin by writing $F+\Delta F$ as

$$F+\Delta F=-\frac{1}{\beta}\ln\int e^{-\beta H_0}e^{-\beta(H_A+\epsilon\Delta H_A)}d\Omega(P). \tag{2.13}$$

$\Delta F$ is given by all terms which are at least linear in $\epsilon$, and $\epsilon$ can be set equal to unity after this identification is made. We rewrite Eq. (2.13) as

$$\begin{aligned}F+\Delta F&=-\frac{1}{\beta}\ln Z_0-\frac{1}{\beta}\ln\int\frac{e^{-\beta H_0}}{Z_0}e^{-\beta(H_A+\epsilon\Delta H_A)}d\Omega(P)\\ &=F_0-\frac{1}{\beta}\ln\langle e^{-\beta(H_A+\epsilon\Delta H_A)}\rangle_0,\end{aligned} \tag{2.14}$$

where $Z_0$ is the partition function in the harmonic approximation and $F_0$ is the corresponding free energy. The logarithm of the thermal average can be expanded in terms of semi-invariants or cumulants[9] with the result that

$$\begin{aligned}\ln\langle&\exp(-\beta\lambda V_3-\beta\lambda^2V_4-\epsilon\beta\lambda\Delta V_3-\epsilon\beta\lambda^2\Delta V_4)\rangle_0\\ &=-\beta\langle\lambda V_3+\lambda^2V_4+\epsilon\lambda\Delta V_3+\epsilon\lambda^2\Delta V_4\rangle_0\\ &\quad+\tfrac{1}{2}\beta^2[\langle(\lambda V_3+\epsilon\lambda\Delta V_3)^2\rangle_0-\langle\lambda V_3+\epsilon\lambda\Delta V_3\rangle_0^2]\\ &\quad+O(\lambda^3),\end{aligned} \tag{2.15}$$

where we have used an obvious extension of the notation of Eq. (2.2).

Since $F_0$ is independent of $\epsilon$, multiplying the expansion in Eq. (2.15) by $-1/\beta$ and picking out the terms depending on $\epsilon$ and of no higher order than $\lambda^2$, we obtain

$$\begin{aligned}\Delta F=\langle\Delta V_3+\Delta V_4\rangle_0-\tfrac{1}{2}\beta[&2\langle V_3\Delta V_3\rangle_0-2\langle V_3\rangle_0\langle\Delta V_3\rangle_0\\ &+\langle(\Delta V_3)^2\rangle_0-\langle\Delta V_3\rangle_0^2].\end{aligned} \tag{2.16}$$

The nonvanishing thermal averages are straightforward to evaluate with the aid of Eq. (2.9). However, there are two considerations which further reduce the number of terms which we have to consider explicitly.

The first of these is the equation

$$\Phi(\mathbf{0}j;\mathbf{k}j';-\mathbf{k}j')=0. \tag{2.17}$$

This result holds for all Bravais lattices. It also holds for lattices with a basis provided that the position of each atom is at a center of inversion symmetry. It is quoted without proof by Peierls,[10] and an explicit proof has been given by Sullivan, Maradudin, and Wallis.[11] It has the consequence that

$$\langle V_3\Delta V_3\rangle_0=\langle\Delta V_3\rangle_0=0. \tag{2.18}$$

Furthermore, it is also true that

$$\langle V_3\rangle_0=0. \tag{2.19}$$

We are thus left with

$$\Delta F=\langle\Delta V_4\rangle_0-\tfrac{1}{2}\beta\langle(\Delta V_3)^2\rangle_0 \tag{2.20}$$

$$\begin{aligned}&=-\frac{1}{4N}\sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3\mathbf{k}_4}\sum_{j_1j_2j_3j_4}\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4)\Phi(\mathbf{k}_1j_1;\mathbf{k}_2j_2;\mathbf{k}_3j_3;\mathbf{k}_4j_4)A(\mathbf{k}_3j_3)A(\mathbf{k}_4j_4)\frac{kT}{\omega^2(\mathbf{k}_1j_1)}\Delta(\mathbf{k}_1+\mathbf{k}_2)\delta_{j_1j_2}\\ &\quad-\frac{\beta}{72N}\sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}\sum_{j_1j_2j_3}\sum_{\mathbf{k}_4\mathbf{k}_5\mathbf{k}_6}\sum_{j_4j_5j_6}\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)\Delta(\mathbf{k}_4+\mathbf{k}_5+\mathbf{k}_6)\Phi(\mathbf{k}_1j_1;\mathbf{k}_2j_2;\mathbf{k}_3j_3)\\ &\quad\times\Phi(\mathbf{k}_4j_4;\mathbf{k}_5j_5;\mathbf{k}_6j_6)\Bigg\{-9A(\mathbf{k}_3j_3)A(\mathbf{k}_6j_6)\frac{2(kT)^2}{\omega^2(\mathbf{k}_1j_1)\omega^2(\mathbf{k}_2j_2)}\Delta(\mathbf{k}_1+\mathbf{k}_4)\Delta(\mathbf{k}_2+\mathbf{k}_5)\delta_{j_1j_4}\delta_{j_2j_5}\\ &\qquad\qquad+9A(\mathbf{k}_2j_2)A(\mathbf{k}_3j_3)A(\mathbf{k}_5j_5)A(\mathbf{k}_6j_6)\frac{kT}{\omega^2(\mathbf{k}_1j_1)}\Delta(\mathbf{k}_1+\mathbf{k}_4)\delta_{j_1j_4}\Bigg\}.\end{aligned} \tag{2.21}$$

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[8] L. Van Hove, "Selected Topics in the Quantum Statistics of Interacting Particles," Lecture Notes, University of Washington, Seattle, Washington, 1958; Tech. Rept. No. 11, Solid State and Molecular Theory Group, MIT, Vol. I, March, 1959.

[9] M. G. Kendall and A. Stuart, *The Advanced Theory of Statistics* (Charles Griffin and Company, Ltd., London, 1958), Chap. 3; See also R. Brout, Phys. Rev. **115**, 824 (1959).

[10] R. E. Peierls, *Quantum Theory of Solids* (Oxford University Press, Oxford, 1955), p. 37 second footnote.

[11] J. Sullivan, A. A. Maradudin, and R. F. Wallis (to be published).

The second simplification arises from the fact that we are calculating the Debye-Waller factor, which arises from the zero-phonon part of $\Delta F$. These are the terms which are independent of both $l$ and $l'$. These indices appear only in the $\{A(\mathbf{k}j)\}$. There are two types of products of the $\{A(\mathbf{k}j)\}$ which are independent of both $l$ and $l'$. The first type consists of products in which the $\mathbf{k}$ vectors are paired two by two. It follows from Eq. (2.4) that a product such as $A(\mathbf{k}j)A(-\mathbf{k}j')$ is independent of $l$ and $l'$. Clearly such pairings can occur only in terms containing an even number of $A(\mathbf{k}j)$ factors.

The second kind of product of the $A(\mathbf{k}j)$ which gives contributions independent of both $l$ and $l'$ is that in which the $\Delta(\mathbf{k}_1+\mathbf{k}_2+\cdots+\mathbf{k}_s)$ function multiplying the product causes the exponential

$$\exp[2\pi i(\mathbf{k}_1+\mathbf{k}_2+\cdots+\mathbf{k}_s)\cdot\mathbf{x}(l)]$$

arising in the product of the $A(\mathbf{k}j)$ to equal unity.

For example, we consider the two terms making up the constant $A$ in Eq. (2.8):

$$A=\frac{-i}{6\sqrt{N}}\sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}\sum_{j_1j_2j_3}\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)\Phi(\mathbf{k}_1j_1;\,\mathbf{k}_2j_2;\,\mathbf{k}_3j_3)A(\mathbf{k}_1j_1)A(\mathbf{k}_2j_2)A(\mathbf{k}_3j_3)$$
$$+\frac{1}{24N}\sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3\mathbf{k}_4}\sum_{j_1j_2j_3j_4}\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4)\Phi(\mathbf{k}_1j_1;\,\mathbf{k}_2j_2;\,\mathbf{k}_3j_3;\,\mathbf{k}_4j_4)A(\mathbf{k}_1j_1)A(\mathbf{k}_2j_2)A(\mathbf{k}_3j_3)A(\mathbf{k}_4j_4).\quad(2.22)$$

The product of three $A(\mathbf{k}j)$ in the first term contributes two terms proportional, respectively, to

$$+\exp[-2\pi i(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)\cdot\mathbf{x}(l)]\quad\text{and}\quad-\exp[-2\pi i(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)\cdot\mathbf{x}(l')].$$

Because of the $\Delta$-function restriction on the sum of the wave vectors, these two terms equal $+1$ and $-1$, respectively, and hence cancel. The remaining six terms in this product depend explicitly on $l$ and $l'$. Thus, this term does not contribute to the Debye-Waller factor.

The second term in Eq. (2.22), however, does yield a nonvanishing contribution to the Debye-Waller factor which is given by

$$\frac{1}{12\beta^3N^3M^2}\sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3\mathbf{k}_4}\sum_{j_1j_2j_3j_4}\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4)\Phi(\mathbf{k}_1j_1;\,\mathbf{k}_2j_2;\,\mathbf{k}_3j_3;\,\mathbf{k}_4j_4)$$
$$\times\frac{[\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_1j_1)][\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_2j_2)][\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_3j_3)][\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_4j_4)]}{\omega^2(\mathbf{k}_1j_1)\omega^2(\mathbf{k}_2j_2)\omega^2(\mathbf{k}_3j_3)\omega^2(\mathbf{k}_4j_4)}.\quad(2.23)$$

In the same way, the only contributions to the Debye-Waller factor arising from the terms in Eq. (2.21) are

$$-\frac{1}{2\beta^2N^2M}\sum_{\mathbf{k}_1\mathbf{k}_2}\sum_{j_1j_2j_3}\frac{\Phi(\mathbf{k}_1j_1;\,-\mathbf{k}_1j_1;\,\mathbf{k}_2j_2;\,-\mathbf{k}_2j_3)}{\omega^2(\mathbf{k}_1j_1)}\,\frac{[\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_2j_2)][\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_2j_3)]}{\omega^2(\mathbf{k}_2j_2)\omega^2(\mathbf{k}_2j_3)}$$
$$+\frac{1}{2\beta^2N^2M}\sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}\sum_{j_1j_2j_3j_4}\frac{\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)\Phi(\mathbf{k}_1j_1;\,\mathbf{k}_2j_2;\,\mathbf{k}_3j_3)\Phi(-\mathbf{k}_1j_1;\,-\mathbf{k}_2j_2;\,-\mathbf{k}_3j_4)}{\omega^2(\mathbf{k}_1j_1)\omega^2(\mathbf{k}_2j_2)}\,\frac{[\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_3j_3)][\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_3j_4)]}{\omega^2(\mathbf{k}_3j_3)\omega^2(\mathbf{k}_3j_4)}$$
$$-\frac{1}{4\beta^3N^3M^2}\sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}\sum_{j_1j_2j_3}\sum_{\mathbf{k}_5\mathbf{k}_6}\sum_{j_5j_6}\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)\Delta(-\mathbf{k}_1+\mathbf{k}_5+\mathbf{k}_6)\frac{\Phi(\mathbf{k}_1j_1;\,\mathbf{k}_2j_2;\,\mathbf{k}_3j_3)\Phi(-\mathbf{k}_1j_1;\,\mathbf{k}_5j_5;\,\mathbf{k}_6j_6)}{\omega^2(\mathbf{k}_1j_1)}$$
$$\times\frac{[\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_2j_2)][\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_3j_3)][\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_5j_5)][\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_6j_6)]}{\omega^2(\mathbf{k}_2j_2)\omega^2(\mathbf{k}_3j_3)\omega^2(\mathbf{k}_5j_5)\omega^2(\mathbf{k}_6j_6)}.\quad(2.24)$$

Combining this result with the contribution given by Eq. (2.23) and the harmonic result, Eq. (1.14), we can order the terms in $2M$ in increasing powers of the temperature:

$$2M=2M_0+2M_1+2M_2+2M_3+2M_4,\quad(2.25)$$

$$2M_0=\frac{kT}{NM}\sum_{\mathbf{k}j}\frac{[\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}j)]^2}{\omega^2(\mathbf{k}j)},\quad(2.26)$$

$$2M_1=-\frac{(kT)^2}{2N^2M}\sum_{\mathbf{k}_1\mathbf{k}_2}\sum_{j_1j_2j_3}\frac{\Phi(\mathbf{k}_1j_1;\,-\mathbf{k}_1j_1;\,\mathbf{k}_2j_2;\,-\mathbf{k}_2j_3)}{\omega^2(\mathbf{k}_1j_1)}\frac{[\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_2j_2)][\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_2j_3)]}{\omega^2(\mathbf{k}_2j_2)\omega^2(\mathbf{k}_2j_3)},\tag{2.27}$$

$$2M_2=\frac{(kT)^2}{2N^2M}\sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}\sum_{j_1j_2j_3j_4}\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)\times\frac{\Phi(\mathbf{k}_1j_1;\,\mathbf{k}_2j_2;\,\mathbf{k}_3j_3)\Phi(-\mathbf{k}_1j_1;\,-\mathbf{k}_2j_2;\,-\mathbf{k}_3j_4)}{\omega^2(\mathbf{k}_1j_1)\omega^2(\mathbf{k}_2j_2)}\frac{[\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_3j_3)][\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_3j_4)]}{\omega^2(\mathbf{k}_3j_3)\omega^2(\mathbf{k}_3j_4)},\tag{2.28}$$

$$2M_3=\frac{(kT)^3}{12N^3M^2}\sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3\mathbf{k}_4}\sum_{j_1j_2j_3j_4}\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4)\Phi(\mathbf{k}_1j_1;\,\mathbf{k}_2j_2;\,\mathbf{k}_3j_3;\,\mathbf{k}_4j_4)\times\frac{[\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_1j_1)][\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_2j_2)][\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_3j_3)][\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_4j_4)]}{\omega^2(\mathbf{k}_1j_1)\omega^2(\mathbf{k}_2j_2)\omega^2(\mathbf{k}_3j_3)\omega^2(\mathbf{k}_4j_4)},\tag{2.29}$$

$$2M_4=-\frac{(kT)^3}{4N^3M^2}\sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}\sum_{j_1j_2j_3}\sum_{\mathbf{k}_5\mathbf{k}_6}\sum_{j_5j_6}\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)\Delta(-\mathbf{k}_1+\mathbf{k}_5+\mathbf{k}_6)\frac{\Phi(\mathbf{k}_1j_1;\,\mathbf{k}_2j_2;\,\mathbf{k}_3j_3)}{\omega^2(\mathbf{k}_1j_1)}\times\Phi(-\mathbf{k}_1j_1;\,\mathbf{k}_5j_5;\,\mathbf{k}_6j_6)\frac{[\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_2j_2)][\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_3j_3)][\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_5j_5)][\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_6j_6)]}{\omega^2(\mathbf{k}_2j_2)\omega^2(\mathbf{k}_3j_3)\omega^2(\mathbf{k}_5j_5)\omega^2(\mathbf{k}_6j_6)}.\tag{2.30}$$

These five terms exhaust the contributions to $2M$ which are $O(\lambda^2)$ and lower.

It is not difficult to show that the contributions to $2M$ which are given by $2M_0+2M_1+2M_2$ are just given by

$$2M_0+2M_1+2M_2=\langle(\boldsymbol{\kappa}\cdot\mathbf{u})^2\rangle.\tag{2.31}$$

This result, together with Eq. (2.25), means that unlike the result for a harmonic crystal the Debye-Waller factor for an anharmonic crystal is no longer just $\exp[-\langle(\boldsymbol{\kappa}\cdot\mathbf{u})^2\rangle]$, where the average is evaluated in the canonical ensemble of the anharmonic crystal. The exponent contains additional terms which are given by $2M_3+2M_4$. These terms we call "anomalous." They can be shown to be given by

$$2M_3+2M_4=-\tfrac{1}{12}[\langle(\boldsymbol{\kappa}\cdot\mathbf{u})^2\rangle-3\langle(\boldsymbol{\kappa}\cdot\mathbf{u})^2\rangle^2],\tag{2.32}$$

where we have retained only terms up to $O(\lambda^2)$ on the right side of this equation.

We now express each of these contributions in terms of a simple model of a three-dimensional crystal.

## III. EVALUATION OF THE DEBYE-WALLER FACTOR

In order to carry out a quantitative calculation of the cubic and quartic anharmonic contributions for a three-dimensional crystal, we need a model of the crystal. We adopt here the nearest-neighbor central force model of a face-centered cubic crystal which has been employed in an earlier paper in this series.[12] This model is discussed extensively in reference 12 so that we will not discuss its properties here, but will merely take over those results of this reference which are relevant to the present calculation.

We begin with Eq. (2.26). As we say in the Introduction, this expression reduces in the case of cubic crystals to

$$2M_0=\kappa^2\frac{kT}{3NM}\sum_{\mathbf{k}j}\frac{1}{\omega^2(\mathbf{k}j)}.\tag{3.1}$$

The sum in Eq. (3.1) has been evaluated elsewhere for the present model[13] with the result that

$$\sum_{\mathbf{k}j}\frac{1}{\omega^2(\mathbf{k}j)}=\frac{10.0584N}{\omega_L^2}=\frac{1.2573NM}{\phi''(r_0)},\tag{3.2}$$

where $\omega_L$ is the maximum frequency of the crystal. Using this value we obtain for the harmonic contribution to the Debye-Waller factor

$$2M_0=\kappa^2\frac{kT}{M\omega_L^2}(3.3528).\tag{3.3}$$

Turning now to Eq. (2.27) and using the fact that[12]

$$\Phi(\mathbf{k}_1j_1;\,\mathbf{k}_2j_2;\,\mathbf{k}_3j_3;\,\mathbf{k}_4j_4)=\frac{\phi^{\text{iv}}(r_0)}{2M^2r_0^4}\sum_{l,\text{n.n.}}[\mathbf{x}(l)\cdot\mathbf{e}(\mathbf{k}_1j_1)][\mathbf{x}(l)\cdot\mathbf{e}(\mathbf{k}_2j_2)]\times[\mathbf{x}(l)\cdot\mathbf{e}(\mathbf{k}_3j_3)][\mathbf{x}(l)\cdot\mathbf{e}(\mathbf{k}_4j_4)](1-e^{-2\pi i\mathbf{k}_1\cdot\mathbf{x}(l)})(1-e^{-2\pi i\mathbf{k}_2\cdot\mathbf{x}(l)})(1-e^{-2\pi i\mathbf{k}_3\cdot\mathbf{x}(l)})(1-e^{-2\pi i\mathbf{k}_4\cdot\mathbf{x}(l)}),\tag{3.4}$$

where $\phi(r)$ is the energy of interaction between a pair of atoms separated by a distance $r$, $r_0$ is the nearest-neighbor

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[12] A. A. Maradudin, P. A. Flinn, and R. A. Coldwell-Horsfall, Ann. Phys. (N. Y.) **15**, 360 (1961).

[13] P. A. Flinn and A. A. Maradudin, Ann. Phys. (N. Y.) **18**, 81 (1962).

separation, and where the vector $\mathbf{x}(l)$ runs over the twelve nearest neighbors to a given lattice point, we obtain

$$2M_1=-\frac{4(kT)^2}{N^2M^3}\frac{\phi^{\mathrm{iv}}(r_0)}{r_0^4}\sum_{l,\mathrm{n.n.}}\sum_{\mathbf{k}_1j_1}\frac{[\mathbf{x}(l)\cdot\mathbf{e}(\mathbf{k}_1j_1)]^2\sin^2\pi\mathbf{k}_1\cdot\mathbf{x}(l)}{\omega^2(\mathbf{k}_1j_1)}$$
$$\times\sum_{\mathbf{k}_2j_2j_3}\sin^2[\pi\mathbf{k}_2\cdot\mathbf{x}(l)]\frac{[\mathbf{x}(l)\cdot\mathbf{e}(\mathbf{k}_2j_2)][\mathbf{x}(l)\cdot\mathbf{e}(\mathbf{k}_2j_3)][\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_2j_2)][\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_2j_3)]}{\omega^2(\mathbf{k}_2j_2)\omega^2(\mathbf{k}_2j_3)}. \qquad (3.5)$$

The sum over $\mathbf{k}_1$ and $j_1$ is readily shown to be independent of $l$ and has the value[12]

$$\left(\frac{a_0}{2}\right)^2\sum_{\mathbf{k}j}\frac{[e_x(\mathbf{k}j)+e_y(\mathbf{k}j)]^2}{\omega^2(\mathbf{k}j)}\sin^2[\tfrac{1}{2}\pi a_0(k_x+k_y)]=\frac{a_0}{16}\frac{NM}{\phi''(r_0)}, \qquad (3.6)$$

where $a_0=\sqrt{2}r_0$ is the lattice parameter.

With the aid of this result the expression for $2M_1$ becomes

$$2M_1=-\frac{1}{2}\frac{(kT)^2}{NM^2}\frac{1}{r_0^2}\frac{\phi^{\mathrm{iv}}(r_0)}{\phi''(r_0)}\sum_{l,\mathrm{n.n.}}\sum_{\mathbf{k}_2j_2j_3}\frac{[\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_2j_2)][\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_2j_3)]}{\omega^2(\mathbf{k}_2j_2)\omega^2(\mathbf{k}_2j_3)}[\mathbf{x}(l)\cdot\mathbf{e}(\mathbf{k}_2j_2)][\mathbf{x}(l)\cdot\mathbf{e}(\mathbf{k}_2j_3)]\sin^2\pi\mathbf{k}_2\cdot\mathbf{x}(l). \qquad (3.7)$$

At this point it is convenient to carry out the sum over $l$ and the use cubic symmetry in reducing the results. The double sum in Eq. (3.7) thus becomes explicitly

$$2\left(\frac{a_0}{2}\right)^2\sum_{\mathbf{k}_2j_2j_3}\frac{[\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_2j_2)][\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_2j_3)]}{\omega^2(\mathbf{k}_2j_2)\omega^2(\mathbf{k}_2j_3)}\{[e_x(\mathbf{k}_2j_2)+e_y(\mathbf{k}_2j_2)][e_x(\mathbf{k}_2j_3)+e_y(\mathbf{k}_2j_3)]\sin^2[\tfrac{1}{2}\pi a_0(k_{2x}+k_{2y})]$$
$$+[e_x(\mathbf{k}_2j_2)-e_y(\mathbf{k}_2j_2)][e_x(\mathbf{k}_2j_3)-e_y(\mathbf{k}_2j_3)]\sin^2[\tfrac{1}{2}\pi a_0(k_{2x}-k_{2y})]+[e_y(\mathbf{k}_2j_2)+e_z(\mathbf{k}_2j_2)][e_y(\mathbf{k}_2j_3)$$
$$+e_z(\mathbf{k}_2j_3)]\sin^2[\tfrac{1}{2}\pi a_0(k_{2y}+k_{2z})]+[e_y(\mathbf{k}_2j_2)-e_z(\mathbf{k}_2j_2)][e_y(\mathbf{k}_2j_3)-e_z(\mathbf{k}_2j_3)]\sin^2[\tfrac{1}{2}\pi a_0(k_{2y}-k_{2z})]$$
$$+[e_z(\mathbf{k}_2j_2)+e_x(\mathbf{k}_2j_2)][e_z(\mathbf{k}_2j_3)+e_x(\mathbf{k}_2j_3)]\sin^2[\tfrac{1}{2}\pi a_0(k_{2z}+k_{2x})]+[e_z(\mathbf{k}_2j_2)-e_x(\mathbf{k}_2j_2)][e_z(\mathbf{k}_2j_3)$$
$$-e_x(\mathbf{k}_2j_3)]\sin^2[\tfrac{1}{2}\pi a_0(k_{2z}-k_{2x})]\}. \qquad (3.8)$$

We now use the transformation properties of the eigenvectors and cubic symmetry to reduce this expression. The transformation property of the eigenvectors that we use the most can be expressed as

$$\mathbf{e}(\mathbf{k}\tilde{A}j)=A\,\mathbf{e}(\mathbf{k}j), \qquad (3.9)$$

where $A$ represents a real orthogonal transformation which takes the reciprocal lattice into itself. In writing Eq. (3.9) in the form given we are expressing $\mathbf{k}$ as a row vector and $\mathbf{e}(\mathbf{k}j)$ as a column vector. The proof of Eq. (3.9) follows from the transformation properties of the second-order (harmonic) atomic force constants[14] and of the dynamical matrix, and are not given here.

Since we are primarily interested in evaluating $2M$ for a cubic Bravais crystal in this paper, the particular cases of Eq. (3.9) which we will use are of the type

$$e_x(k_y,k_z,k_xj)=e_y(k_x,k_y,k_zj),\ \text{etc.}, \qquad (3.10\text{a})$$
$$e_x(-k_x,k_y,k_zj)=-e_x(k_x,k_y,k_zj), \qquad (3.10\text{b})$$
$$e_y(-k_x,k_y,k_zj)=e_y(k_x,k_y,k_zj). \qquad (3.10\text{c})$$

Along special directions in $\mathbf{k}$ space such as the [100] and [111] directions the eigenvectors are indeterminate due to the degeneracy of the frequencies belonging to the two transverse modes. In such cases the relations among the components of the eigenvectors implied by Eq. (3.10) may or may not be satisfied. This, however, does not matter since any two normalized vectors which are perpendicular to each other and to the eigenvector of the longitudinal mode are acceptable eigenvectors for the transverse modes, even if their components do not satisfy Eq. (3.10). It should also be remarked that there is a fundamental indeterminacy in the sign of the right-hand side of Eq. (3.9): it could equally well be negative. However, since no eigenvector ever occurs singly but is always paired with another belonging to the same $\mathbf{k}$ value, this indeterminacy of sign never affects any of our answers.

If we now apply Eqs. (3.9) and (3.10) to the expression (3.8), we can simplify it to

$$2\left(\frac{a_0}{2}\right)^2\sum_{\mathbf{k}_2j_2j_3}\frac{2\kappa^2[\mathbf{e}(\mathbf{k}_2j_2)\cdot\mathbf{e}(\mathbf{k}_2j_3)]}{\omega^2(\mathbf{k}_2j_2)\omega^2(\mathbf{k}_2j_3)}[e_x(\mathbf{k}_2j_2)+e_y(\mathbf{k}_2j_2)][e_x(\mathbf{k}_2j_3)+e_y(\mathbf{k}_2j_3)]\sin^2[\tfrac{1}{2}\pi a_0(k_{2x}+k_{2y})]$$
$$=\kappa^2a_0^2\sum_{\mathbf{k}_2j_2}\frac{[e_x(\mathbf{k}_2j_2)+e_y(\mathbf{k}_2j_2)]^2}{\omega^4(\mathbf{k}_2j_2)}\sin^2[\tfrac{1}{2}\pi a_0(k_{2x}+k_{2y})]. \qquad (3.11)$$

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[14] G. Leibfried, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1955), Vol. 7, part 1, p. 104.

In Appendix A it is shown that this sum is equal to

$$\frac{2}{3}\frac{\kappa^2 a_0^2}{\omega_L^2}\sum_{\mathbf{k}j}\frac{1}{\omega^2(\mathbf{k}j)}=\kappa^2 a_0^2\frac{M}{12\phi''(r_0)}\sum_{\mathbf{k}j}\frac{1}{\omega^2(\mathbf{k}j)}. \tag{3.12}$$

Combining the results expressed by Eqs. (3.7), (3.11), (3.12), and (3.2) we have, finally, that

$$2M_1=-6.7056\kappa^2\frac{(kT)^2}{M^2\omega_L^4}\frac{\phi^{\mathrm{iv}}(r_0)}{\phi''(r_0)}. \tag{3.13}$$

We turn now to the evaluation of $2M_2$ which is given by

$$2M_2=\frac{(kT)^2}{2N^2M}\sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}\sum_{j_1j_2j_3j_4}\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)\frac{\Phi(\mathbf{k}_1j_1;\,\mathbf{k}_2j_2;\,\mathbf{k}_3j_3)\Phi(-\mathbf{k}_1j_1;\,-\mathbf{k}_2j_2;\,-\mathbf{k}_3j_4)}{\omega^2(\mathbf{k}_1j_1)\omega^2(\mathbf{k}_2j_2)}\frac{[\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_3j_3)][\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_3j_4)]}{\omega^2(\mathbf{k}_3j_3)\omega^2(\mathbf{k}_3j_4)}. \tag{3.14}$$

In this section we merely simplify this expression somewhat and defer a discussion of its numerical evaluation to Sec. VI.

We replace $\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)$ by its representation as a Fourier series,

$$\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)=(1/N)\textstyle\sum_l \exp[2\pi i(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)\cdot\mathbf{x}(l)], \tag{3.15}$$

and introduce the explicit expression for $\Phi(\mathbf{k}_1j_1;\,\mathbf{k}_2j_2;\,\mathbf{k}_3j_3)$ appropriate to our model[12]:

$$\Phi(\mathbf{k}_1j_1;\,\mathbf{k}_2j_2;\,\mathbf{k}_3j_3)=(2i)^3\frac{\phi'''(r_0)}{2(2M)^{3/2}}\sum_{\mathrm{n.n.}}[\mathbf{n}\cdot\mathbf{e}(\mathbf{k}_1j_1)][\mathbf{n}\cdot\mathbf{e}(\mathbf{k}_2j_2)][\mathbf{n}\cdot\mathbf{e}(\mathbf{k}_3j_3)]$$
$$\times\exp[-\tfrac{1}{2}\pi ia_0(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)\cdot\mathbf{n}]\sin(\tfrac{1}{2}\pi a_0\mathbf{k}_1\cdot\mathbf{n})\sin(\tfrac{1}{2}\pi a_0\mathbf{k}_2\cdot\mathbf{n})\sin(\tfrac{1}{2}\pi a_0\mathbf{k}_3\cdot\mathbf{n}), \tag{3.16}$$

where we have introduced the dimensionless vector with integer components,

$$\mathbf{x}(l)=\tfrac{1}{2}a_0\mathbf{n}. \tag{3.17}$$

The sum over $\mathbf{n}$ extends over the twelve nearest neighbors to a given lattice point.

If we substitute Eqs. (3.15) and (3.16) into Eq. (3.14) it becomes

$$2M_2=(kT)^2\frac{[\phi'''(r_0)]^2}{N^3M^4}\sum_l\sum_{\mathbf{n}_1\mathbf{n}_2\,\mathrm{n.n.}}\sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}\sum_{j_1j_2j_3j_4}\exp[2\pi i(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)\cdot\mathbf{x}(l)]\exp[-\tfrac{1}{2}\pi ia_0(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)\cdot(\mathbf{n}_1-\mathbf{n}_2)]$$
$$\times\frac{[\mathbf{n}_1\cdot\mathbf{e}(\mathbf{k}_1j_1)][\mathbf{n}_2\cdot\mathbf{e}(\mathbf{k}_1j_1)][\mathbf{n}_1\cdot\mathbf{e}(\mathbf{k}_2j_2)][\mathbf{n}_2\cdot\mathbf{e}(\mathbf{k}_2j_2)][\mathbf{n}_1\cdot\mathbf{e}(\mathbf{k}_3j_3)][\mathbf{n}_2\cdot\mathbf{e}(\mathbf{k}_3j_4)]}{\omega^2(\mathbf{k}_1j_1)\omega^2(\mathbf{k}_2j_2)\omega^2(\mathbf{k}_3j_3)\omega^2(\mathbf{k}_3j_4)}\sin(\tfrac{1}{2}\pi a_0\mathbf{k}_1\cdot\mathbf{n}_1)$$
$$\times\sin(\tfrac{1}{2}\pi a_0\mathbf{k}_1\cdot\mathbf{n}_2)\quad\sin(\tfrac{1}{2}\pi a_0\mathbf{k}_2\cdot\mathbf{n}_1)\sin(\tfrac{1}{2}\pi a_0\mathbf{k}_2\cdot\mathbf{n}_2)\sin(\tfrac{1}{2}\pi a_0\mathbf{k}_3\cdot\mathbf{n}_1)\sin(\tfrac{1}{2}\pi a_0\mathbf{k}_3\cdot\mathbf{n}_2)[\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_3j_3)][\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_3j_4)]. \tag{3.18}$$

In the product $[\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_3j_3)][\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_3j_4)]$ there occur two basically different kinds of terms, namely, $\kappa_x^2e_x(\mathbf{k}_3j_3)\times e_x(\mathbf{k}_3j_4)$ and $\kappa_x\kappa_ye_x(\mathbf{k}_3j_3)e_y(\mathbf{k}_3j_4)$. We now show that the second kind of term gives a vanishing contribution to $2M_2$, while the first kind of term has the same value if $e_x(\mathbf{k}_3j_3)e_x(\mathbf{k}_3j_4)$ is replaced by either $e_y(\mathbf{k}_3j_3)e_y(\mathbf{k}_3j_4)$ or $e_z(\mathbf{k}_3j_3)e_z(\mathbf{k}_3j_4)$.

We begin by replacing the product $[\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_3j_3)]\times[\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_3j_4)]$ in Eq. (3.18) by one of its terms, viz., $\kappa_x^2e_x(\mathbf{k}_3j_3)e_x(\mathbf{k}_3j_4)$. Since, in the sum over $\mathbf{k}_3$, $k_{3x}$, $k_{3y}$, and $k_{3z}$ are dummy variables, each of which assumes the same values as the others, we can relabel them $k_{3y}$, $k_{3z}$, and $k_{3x}$, respectively, without altering the value of the sum. However, in view of Eq. (3.10) we see that the factor $\kappa_x^2e_x(k_{3y},k_{3z},k_{3x}j_3)e_x(k_{3y},k_{3z},k_{3x}j_4)$ is equal to

$$\kappa_x^2e_y(k_{3x},k_{3y},k_{3z}j_3)e_y(k_{3x},k_{3y},k_{3z}j_4).$$

We now relabel $(k_{1x},k_{1y},k_{1z})$ and $(k_{2x},k_{2y},k_{2z})$ in Eq. (3.18) as $(k_{1y},k_{1z},k_{1x})$ and $(k_{2y},k_{2z},k_{2x})$, respectively. The sum is invariant against this change. If we now replace $(n_{1x},n_{1y},n_{1z})$ by $(n_{1y},n_{1z},n_{1x})$, respectively, and treat similarly the components of $\mathbf{n}_2$ and $\mathbf{x}(l)$, the value of the sum is not changed, but the coefficient multiplying $\kappa_x^2e_y(\mathbf{k}_3j_3)e_y(\mathbf{k}_3j_4)$ is the same as that which multiplied $\kappa_x^2e_x(\mathbf{k}_3j_3)e_x(\mathbf{k}_3j_4)$ when we started.

It only remains to show that the terms proportional to $\kappa_x\kappa_y$, $\kappa_y\kappa_z$, and $\kappa_z\kappa_x$ vanish. We merely sketch the proof. We begin by replacing the factor $[\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_3j_3)][\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_3j_4)]$

in Eq. (3.18) by $\kappa_x\kappa_y e_x(\mathbf{k}_3j_3)e_y(\mathbf{k}_3j_4)$, and then replace $k_{3x}$ by $-k_{3x}$ as a summation variable. The value of the sum cannot be altered by this replacement. However, in view of Eq. (3.10) the effect of this step is to change the sign of the right-hand side of Eq. (3.18), and to replace $k_{3x}$ by $-k_{3x}$ in all the factors of the summand except in the factor $\kappa_x\kappa_y e_x(\mathbf{k}_3j_3)e_y(\mathbf{k}_3j_4)$. But if we now replace the summation variables $k_{1x}$ and $k_{2x}$ by $-k_{1x}$ and $-k_{2x}$, respectively, and replace $n_{1x}$, $n_{2x}$, $x_x(l)$ by their negatives in the sums over these variables, neither of which steps can alter the value of the sums, we end up with an expression which is the negative of the sum we started with. This implies the vanishing of the sum.

Thus, the terms in Eq. (3.18) proportional to $\kappa_x^2$, $\kappa_y^2$, $\kappa_z^2$ can be combined to yield

$$2M_2=\tfrac{1}{3}\kappa^2(kT)^2\frac{[\phi'''(r_0)]^2}{N^3M^4}\sum_{l}\sum_{\mathbf{n}_1\mathbf{n}_2\,\mathrm{n.n.}}\sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}\sum_{j_1j_2j_3}\exp[2\pi i(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)\cdot\mathbf{x}(l)]$$
$$\times\frac{[\mathbf{n}_1\cdot\mathbf{e}(\mathbf{k}_1j_1)][\mathbf{n}_2\cdot\mathbf{e}(\mathbf{k}_1j_1)][\mathbf{n}_1\cdot\mathbf{e}(\mathbf{k}_2j_2)][\mathbf{n}_2\cdot\mathbf{e}(\mathbf{k}_2j_2)][\mathbf{n}_1\cdot\mathbf{e}(\mathbf{k}_3j_3)][\mathbf{n}_2\cdot\mathbf{e}(\mathbf{k}_3j_3)]}{\omega^2(\mathbf{k}_1j_1)\omega^2(\mathbf{k}_2j_2)\omega^4(\mathbf{k}_3j_3)}$$
$$\times\exp[-\tfrac{1}{2}\pi ia_0(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)\cdot(\mathbf{n}_1-\mathbf{n}_2)]\sin(\tfrac{1}{2}\pi a_0\mathbf{k}_1\cdot\mathbf{n}_1)\sin(\tfrac{1}{2}\pi a_0\mathbf{k}_1\cdot\mathbf{n}_2)\sin(\tfrac{1}{2}\pi a_0\mathbf{k}_2\cdot\mathbf{n}_1)$$
$$\times\sin(\tfrac{1}{2}\pi a_0\mathbf{k}_2\cdot\mathbf{n}_2)\sin(\tfrac{1}{2}\pi a_0\mathbf{k}_3\cdot\mathbf{n}_1)\sin(\tfrac{1}{2}\pi a_0\mathbf{k}_3\cdot\mathbf{n}_2),\qquad(3.19)$$

where we have used the orthonormality of eigenvectors belonging to different branches but to the same wave vector. This result can finally be expressed compactly as

$$2M_2=\frac{\kappa^2}{48}\frac{(kT)^2}{N^2}\frac{[\phi'''(r_0)]^2}{[\phi''(r_0)]^4}\sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}\sum_{j_1j_2j_3}\frac{\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)F^2(\mathbf{k}_1j_1;\,\mathbf{k}_2j_2;\,\mathbf{k}_3j_3)}{\lambda^2(\mathbf{k}_1j_1)\lambda^2(\mathbf{k}_2j_2)\lambda^4(\mathbf{k}_3j_3)},\qquad(3.20)$$

where

$$F(\mathbf{k}_1j_1;\,\mathbf{k}_2j_2;\,\mathbf{k}_3j_3)=\sum_{\mathbf{n},\,\mathrm{n.n.}}\exp(\tfrac{1}{2}\pi ia_0\boldsymbol{\tau}\cdot\mathbf{n})[\mathbf{n}\cdot\mathbf{e}(\mathbf{k}_1j_1)][\mathbf{n}\cdot\mathbf{e}(\mathbf{k}_2j_2)][\mathbf{n}\cdot\mathbf{e}(\mathbf{k}_3j_3)]$$
$$\times\sin(\tfrac{1}{2}\pi a_0\mathbf{k}_1\cdot\mathbf{n})\sin(\tfrac{1}{2}\pi a_0\mathbf{k}_2\cdot\mathbf{n})\sin(\tfrac{1}{2}\pi a_0\mathbf{k}_3\cdot\mathbf{n}).\qquad(3.21)$$

In Eq. (3.20) $\lambda(\mathbf{k}j)$ is a dimensionless frequency which is defined by

$$\omega^2(\mathbf{k}j)=\frac{2\phi''(r_0)}{M}\lambda^2(\mathbf{k}j),\qquad(3.22)$$

and $\boldsymbol{\tau}$ is the translation vector of the reciprocal lattice which satisfies $\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3=\boldsymbol{\tau}$.

We are finally left with the two sums given by Eqs. (2.29) and (2.30) to evaluate. In this section we reduce them to a more manageable form for numerical calculations, and discuss their evaluation in Sec. V.

When we expand the product $[\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_1j_1)][\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_2j_2)]\times[\mathbf{k}\cdot\mathbf{e}(\mathbf{k}_3j_3)][\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_4j_4)]$ in terms of the components of $\boldsymbol{\kappa}$ and the $\mathbf{e}(\mathbf{k}j)$'s, of the 81 terms which result only very few give nonvanishing contributions to $2M_3$ and $2M_4$. These terms are those which are even in $\kappa_x$, $\kappa_y$, $\kappa_z$. That the remaining terms give rise to vanishing contributions follows from the same kinds of manipulations of the various dummy summation variables as were used to establish the analogous result for $2M_2$.

The only terms which survive are those which contain

$$\kappa_x^4e_x(\mathbf{k}_1j_1)e_x(\mathbf{k}_2j_2)e_x(\mathbf{k}_3j_3)e_x(\mathbf{k}_4j_4)$$
$$+\kappa_y^4e_y(\mathbf{k}_1j_1)e_y(\mathbf{k}_2j_2)e_y(\mathbf{k}_3j_3)e_y(\mathbf{k}_4j_4)$$
$$+\kappa_z^4e_z(\mathbf{k}_1j_1)e_z(\mathbf{k}_2j_2)e_z(\mathbf{k}_3j_3)e_z(\mathbf{k}_4j_4),\qquad(3.23)$$

and those which are of the type

$$\kappa_x^2\kappa_y^2e_x(\mathbf{k}_1j_1)e_x(\mathbf{k}_2j_2)e_y(\mathbf{k}_3j_3)e_y(\mathbf{k}_4j_4),$$
$$\kappa_y^2\kappa_z^2e_y(\mathbf{k}_1j_1)e_y(\mathbf{k}_2j_2)e_z(\mathbf{k}_3j_3)e_z(\mathbf{k}_4j_4),\qquad(3.24)$$
$$\kappa_z^2\kappa_x^2e_z(\mathbf{k}_1j_1)e_z(\mathbf{k}_2j_2)e_x(\mathbf{k}_3j_3)e_x(\mathbf{k}_4j_4).$$

In the case of $2M_3$, each of the expressions in Eq. (3.24) is multiplied by a factor of six corresponding to the six equivalent permutations of the $(\mathbf{k}_ij_i)$ among the $x$'s and $y$'s and $z$'s. Their equivalence is a consequence of the invariance of

$$\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4)\Phi(\mathbf{k}_1j_1;\,\mathbf{k}_2j_2;\,\mathbf{k}_3j_3;\,\mathbf{k}_4j_4)$$

against the interchange of any pair of $(\mathbf{k}_ij_i)$.

In the case of $2M_4$ the six terms of each of the three categories displayed in Eq. (3.24) are divided into two groups, containing two and four members, respectively. This is due to the fact that while

$$\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)\Delta(-\mathbf{k}_1+\mathbf{k}_5+\mathbf{k}_6)$$
$$\times\Phi(\mathbf{k}_1j_1;\,\mathbf{k}_2j_2;\,\mathbf{k}_3j_3)\Phi(-\mathbf{k}_1j_1;\,\mathbf{k}_5j_5;\,\mathbf{k}_6j_6)$$

is invariant against an interchange of $(\mathbf{k}_2j_2)$ and $(\mathbf{k}_3j_3)$, it is not invariant against an interchange of $(\mathbf{k}_2j_2)$ and $(\mathbf{k}_5j_5)$.

It is also straightforward to show for both $2M_3$ and $2M_4$, by the appropriate relabeling of the components of the vectors $\mathbf{k}_i$, that the sums multiplying $\kappa_x^4$, $\kappa_y^4$, $\kappa_z^4$ are equal, as are the sums multiplying $\kappa_x^2\kappa_y^2$, $\kappa_y^2\kappa_z^2$, $\kappa_z^2\kappa_x^2$.

After these preliminary comments we turn to an explicit discussion of $2M_3$ and $2M_4$.

We first consider $2M_3$. If we use the result that

$$\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4) = (1/N)\sum_l \exp[2\pi i(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4)\cdot\mathbf{x}(l)], \tag{3.25}$$

together with Eq. (3.4), and make use of the foregoing qualitative results, we have

$$2M_3=\frac{(kT)^3}{96N^4}\frac{\phi^{\text{iv}}(r_0)}{M^4}\{A(\kappa_x^4+\kappa_y^4+\kappa_z^4)+6B(\kappa_x^2\kappa_y^2+\kappa_y^2\kappa_z^2+\kappa_z^2\kappa_x^2)\}, \tag{3.26}$$

where

$$A=\sum_l\sum_{\mathbf{n},\,\text{n.n.}}\left\{\sum_{\mathbf{k}j}e^{2\pi i\mathbf{k}\cdot\mathbf{x}(l)}\frac{[\mathbf{n}\cdot\mathbf{e}(\mathbf{k}j)](1-e^{-\pi i a_0\mathbf{k}\cdot\mathbf{n}})e_x(\mathbf{k}j)}{\omega^2(\mathbf{k}j)}\right\}^4, \tag{3.27a}$$

$$B=\sum_l\sum_{\mathbf{n},\,\text{n.n.}}\left\{\sum_{\mathbf{k}j}e^{2\pi i\mathbf{k}\cdot\mathbf{x}(l)}\frac{[\mathbf{n}\cdot\mathbf{e}(\mathbf{k}j)](1-e^{-\pi i a\mathbf{k}\cdot\mathbf{n}})e_x(\mathbf{k}j)}{\omega^2(\mathbf{k}j)}\right\}^2\left\{\sum_{\mathbf{k}j}e^{2\pi i\mathbf{k}\cdot\mathbf{x}(l)}\frac{[\mathbf{n}\cdot\mathbf{e}(\mathbf{k}j)](1-e^{-\pi i a_0\mathbf{k}\cdot\mathbf{n}})e_y(\mathbf{k}j)}{\omega^2(\mathbf{k}j)}\right\}^2. \tag{3.27b}$$

Since, in general, $6B\neq 2A$, we see from this result that inclusion of the contribution from $2M_3$ to the Debye-Waller factor leads to a result which is no longer isotropic with respect to $\boldsymbol{\kappa}$.

We finally come to the term $2M_4$, which is given by Eq. (2.30). If we use the Fourier representation Eq. (3.15) for each of the $\Delta$ functions appearing in this expression and make use of the symmetry arguments described above, we find that we can write $2M_4$ as

$$-2M_4=\frac{(kT)^3}{128}\frac{[\phi'''(r_0)]^2}{N^5M^5}\{C(\kappa_x^4+\kappa_y^4+\kappa_z^4)+(2D+4E)(\kappa_x^2\kappa_y^2+\kappa_y^2\kappa_z^2+\kappa_z^2\kappa_x^2)\}, \tag{3.28}$$

where

$$C=\sum_{l_1l_2}\sum_{\mathbf{n}_1\mathbf{n}_2,\,\text{n.n.}}\sum_{\mathbf{k}_1j_1}e^{2\pi i\mathbf{k}_1\cdot[\mathbf{x}(l_1)-\mathbf{x}(l_2)]}(1-e^{-\pi i a_0\mathbf{k}_1\cdot\mathbf{n}_1})(1-e^{\pi i a_0\mathbf{k}_1\cdot\mathbf{n}_2})\frac{[\mathbf{n}_1\cdot\mathbf{e}(\mathbf{k}_1j_1)][\mathbf{n}_2\cdot\mathbf{e}(\mathbf{k}_1j_1)]}{\omega^2(\mathbf{k}_1j_1)}$$
$$\times\left\{\sum_{\mathbf{k}j}e^{2\pi i\mathbf{k}\cdot\mathbf{x}(l_1)}[\mathbf{n}_1\cdot\mathbf{e}(\mathbf{k}j)](1-e^{-\pi i a_0\mathbf{k}\cdot\mathbf{n}_1})\frac{e_x(\mathbf{k}j)}{\omega^2(\mathbf{k}j)}\right\}^2\left\{\sum_{\mathbf{k}j}e^{2\pi i\mathbf{k}\cdot\mathbf{x}(l_2)}[\mathbf{n}_2\cdot\mathbf{e}(\mathbf{k}j)](1-e^{-\pi i a_0\mathbf{k}\cdot\mathbf{n}_2})\frac{e_x(\mathbf{k}j)}{\omega^2(\mathbf{k}j)}\right\}^2, \tag{3.29a}$$

$$D=\sum_{l_1l_2}\sum_{\mathbf{n}_1\mathbf{n}_2,\,\text{n.n.}}\sum_{\mathbf{k}_1j_1}e^{2\pi i\mathbf{k}_1\cdot[\mathbf{x}(l_1)-\mathbf{x}(l_2)]}(1-e^{-\pi i a_0\mathbf{k}_1\cdot\mathbf{n}_1})(1-e^{\pi i a_0\mathbf{k}_1\cdot\mathbf{n}_2})\frac{[\mathbf{n}_1\cdot\mathbf{e}(\mathbf{k}_1j_1)][\mathbf{n}_2\cdot\mathbf{e}(\mathbf{k}_1j_1)]}{\omega^2(\mathbf{k}_1j_1)}$$
$$\times\left\{\sum_{\mathbf{k}j}e^{2\pi i\mathbf{k}\cdot\mathbf{x}(l_1)}[\mathbf{n}_1\cdot\mathbf{e}(\mathbf{k}j)](1-e^{-\pi i a_0\mathbf{k}\cdot\mathbf{n}_1})\frac{e_x(\mathbf{k}j)}{\omega^2(\mathbf{k}j)}\right\}^2\left\{\sum_{\mathbf{k}j}e^{2\pi i\mathbf{k}\cdot\mathbf{x}(l_2)}[\mathbf{n}_2\cdot\mathbf{e}(\mathbf{k}j)](1-e^{\pi i a_0\mathbf{k}\cdot\mathbf{n}_2})\frac{e_y(\mathbf{k}j)}{\omega^2(\mathbf{k}j)}\right\}^2, \tag{3.29b}$$

$$E=\sum_{l_1l_2}\sum_{\mathbf{n}_1\mathbf{n}_2,\,\text{n.n.}}\sum_{\mathbf{k}_1j_1}e^{2\pi i\mathbf{k}_1\cdot[\mathbf{x}(l_1)-\mathbf{x}(l_2)]}(1-e^{-\pi i a_0\mathbf{k}_1\cdot\mathbf{n}_1})(1-e^{\pi i a_0\mathbf{k}_1\cdot\mathbf{n}_2})\frac{[\mathbf{n}_1\cdot\mathbf{e}(\mathbf{k}_1j_1)][\mathbf{n}_2\cdot\mathbf{e}(\mathbf{k}_1j_1)]}{\omega^2(\mathbf{k}_1j_1)}$$
$$\times\sum_{\mathbf{k}_2j_2}e^{2\pi i\mathbf{k}_2\cdot\mathbf{x}(l_1)}[\mathbf{n}_1\cdot\mathbf{e}(\mathbf{k}_2j_2)](1-e^{-\pi i a_0\mathbf{k}_2\cdot\mathbf{n}_1})\frac{e_x(\mathbf{k}_2j_2)}{\omega^2(\mathbf{k}_2j_2)}\sum_{\mathbf{k}_3j_3}e^{2\pi i\mathbf{k}_3\cdot\mathbf{x}(l_1)}[\mathbf{n}_1\cdot\mathbf{e}(\mathbf{k}_3j_3)](1-e^{-\pi i a_0\mathbf{k}_3\cdot\mathbf{n}_1})\frac{e_y(\mathbf{k}_3j_3)}{\omega^2(\mathbf{k}_3j_3)}$$
$$\times\sum_{\mathbf{k}_5j_5}e^{2\pi i\mathbf{k}_5\cdot\mathbf{x}(l_2)}[\mathbf{n}_2\cdot\mathbf{e}(\mathbf{k}_5j_5)](1-e^{-\pi i a_0\mathbf{k}_5\cdot\mathbf{n}_2})\frac{e_x(\mathbf{k}_5j_5)}{\omega^2(\mathbf{k}_5j_5)}\sum_{\mathbf{k}_6j_6}e^{2\pi i\mathbf{k}_6\cdot\mathbf{x}(l_2)}[\mathbf{n}_2\cdot\mathbf{e}(\mathbf{k}_6j_6)](1-e^{-\pi i a_0\mathbf{k}_6\cdot\mathbf{n}_2})\frac{e_y(\mathbf{k}_6j_6)}{\omega^2(\mathbf{k}_6j_6)}. \tag{3.29c}$$

We see that this contribution to the Debye-Waller factor is also not isotropic.

The evaluation of these expressions is discussed in Sec. V.

## IV. THE EFFECT OF THERMAL EXPANSION

We have not as yet considered the effect of the thermal expansion of the crystal on the Debye-Waller factor. This is a comparatively easy correction to make if we are satisfied with an approximate result.

The expression for the Debye-Waller factor in the harmonic approximation, Eq. (3.3), can be written for our model as

$$2M_0=0.4191\kappa^2[kT/\phi''(r_0)], \tag{4.1}$$

where we have used the fact that the maximum frequency of the lattice is

$$\omega_L{}^2=8\phi''(r_0)/M. \tag{4.2}$$

In both of these expressions $r_0$ is the equilibrium value of the nearest neighbor separation at temperature $T$.

In discussing the effects of thermal expansion, it is convenient to expand all quantities about their values in the lattice configuration which corresponds to the minimum of the *potential energy*. This is a unique configuration because it is independent of temperature. If we denote the nearest-neighbor separation corresponding to the minimum of the potential energy by $\bar{r}_0$, then we can write

$$r_0=(1+\epsilon)\bar{r}_0, \tag{4.3}$$

where $\epsilon$ is the linear expansivity of the crystal.

If we substitute Eq. (4.3) into Eq. (4.1) and expand $2M_0$ in powers of $\epsilon$ we obtain

$$2M_0=0.4191\kappa^2\frac{kT}{\phi''(\bar{r}_0)}\left[1-\epsilon\bar{r}_0\frac{\phi'''(\bar{r}_0)}{\phi''(\bar{r}_0)}+O(\epsilon^2)\right]. \tag{4.4}$$

It only remains to determine $\epsilon$ as a function of temperature. We note that since $\phi'''(\bar{r}_0)$ is $O(\lambda)$ we require $\epsilon$ only to $O(\lambda)$ in order to obtain $2M_0$ correct to $O(\lambda^2)$.

The result of reference 12 for the vibrational contribution to the Helmholtz free energy in the high-temperature limit is

$$F(T)=3NkT\ \ln 0.6505\frac{\hbar}{kT}\left(\frac{8\phi''(r_0)}{M}\right)^{1/2}+O(\lambda^2). \tag{4.5}$$

The static lattice contribution to the free energy is

$$U=6N\phi(r_0). \tag{4.6}$$

We expand $U$ about $\bar{r}_0$ up to quadratic terms in $\epsilon$, and expand $F(T)$ up to linear terms:

$$U=6N[\phi(\bar{r}_0)+\tfrac{1}{2}\epsilon^2\bar{r}_0{}^2\phi''(\bar{r}_0)+O(\epsilon^3)], \tag{4.7a}$$

$$F(T)=3NkT\ \ln 0.6505\frac{\hbar}{kT}\left(\frac{8\phi''(\bar{r}_0)}{M}\right)^{1/2}+\epsilon\bar{r}_0\frac{3NkT}{2}\frac{\phi'''(\bar{r}_0)}{\phi''(\bar{r}_0)}+O(\epsilon^2). \tag{4.7b}$$

The equilibrium value of $\epsilon$ at temperature $T$ is obtained by minimizing the sum $U+F(T)$ with respect to $\epsilon$:

$$6N\epsilon\bar{r}_0{}^2\phi''(\bar{r}_0)+\bar{r}_0\frac{3NkT}{2}\frac{\phi'''(\bar{r}_0)}{\phi''(\bar{r}_0)}+\cdots=0.$$

Solving for $\epsilon$ we obtain

$$\epsilon=-\frac{kT}{4\bar{r}_0}\frac{\phi'''(\bar{r}_0)}{[\phi''(\bar{r}_0)]^2}. \tag{4.8}$$

It is not difficult to show that the terms omitted in this result are $O(\lambda^3)$.

We now use Eq. (4.8) in Eq. (4.4) and obtain finally

$$2M_0=0.4191\kappa^2\frac{kT}{\phi''(\bar{r}_0)}+0.1048\kappa^2(kT)^2\frac{[\phi'''(\bar{r}_0)]^2}{[\phi''(\bar{r}_0)]^4}+O(\lambda^2). \tag{4.9}$$

It is not necessary to apply the correction for thermal expansion to the remaining terms in $2M$ since they are already $O(\lambda^2)$. This fact has the further consequence that in evaluating the cubic and quartic anharmonic contributions to $2M$ we must use their values calculated in the configuration corresponding to the minimum of the potential energy, since the corrections to these values are of higher order in $\lambda$ than we are considering here.

It is worth pointing out that if we replace $F(T)$ by the zero-point energy[15]

$$E_0=1.0227N\hbar\left(\frac{8\phi''(r_0)}{M}\right)^{1/2}=N\epsilon_0, \tag{4.10}$$

in the preceding calculations, we find that the value of $\epsilon$ at the absolute zero of temperature is given by

$$\epsilon_0=-\frac{1}{12}\frac{\bar{\epsilon}_0}{\bar{r}_0}\frac{\phi'''(\bar{r}_0)}{[\phi''(\bar{r}_0)]^2}, \tag{4.11}$$

where $\bar{\epsilon}_0$ is the zero-point energy per atom evaluated at the minimum of the potential energy. That $\epsilon_0$ is not zero is a manifestation of the fact that the value of the nearest-neighbor separation even at the absolute zero of temperature is determined by minimizing the total free energy, including zero-point energy, and not just the potential energy.

Finally, we remark that the approximation we have used in obtaining the results of this section is that we have taken the result for the free energy in the harmonic approximation and have evaluated it for an expanded lattice. The correct procedure is to start with a uniformly expanded lattice and evaluate its free energy. This is generally a more difficult calculation to carry out than the calculations we have performed.

However, the results of a rigorous calculation of the shift in phonon frequencies due to thermal expansion, which will be reported elsewhere, show that although the results of the present section were obtained in an approximate manner, they are nevertheless correct for the crystal model with which we work.

## V. EVALUATION OF $2M_3$ AND $2M_4$

The sums $A$, $B$, $C$, $D$, and $E$ which appear in the expressions for $2M_3$ and $2M_4$ are so complicated that it was felt that their exact evaluation, even with the aid

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[15] C. Domb and C. Isenberg (private communication).

of a computer, is impractical at this time. We have accordingly evaluated them by making use of an approximation due to Ludwig.[16] This approximation consists of replacing each factor of $\omega^2(\mathbf{k}j)$ in the denominators of these sums by its average value which is given by

$$\langle\omega^2(\mathbf{k}j)\rangle=\frac{1}{3N}\sum_{\mathbf{k}j}\omega^2(\mathbf{k}j)=\mu_2, \tag{5.1}$$

where $\mu_2$ is the second moment of the frequency spectrum of the crystal in the harmonic approximation. For the present model

$$\mu_2=4\phi''(r_0)/M=\tfrac{1}{2}\omega_L^2, \tag{5.2}$$

where $\omega_L$ is the maximum frequency of the crystal. When this is done the sums can be evaluated in closed form.

To illustrate the procedure we present the evaluation of the sum $A$ in detail and merely list the results for the remaining sums.

After we use Ludwig's approximation, $A$ becomes

$$A=\frac{1}{\mu_2{}^4}\sum_{l}\sum_{\mathrm{n,n.n.}}\{\sum_{\mathbf{k}j}e^{2\pi i\mathbf{k}\cdot\mathbf{x}(l)}e_x(\mathbf{k}j)$$
$$\times[\mathbf{n}\cdot\mathbf{e}(\mathbf{k}j)](1-e^{-\pi ia_0\mathbf{k}\cdot\mathbf{n}})\}^4 \tag{5.3}$$
$$=\frac{1}{\mu_2{}^4}\sum_{l}\sum_{\mathrm{n,n.n.}}\{\sum_{\mathbf{k}}e^{2\pi i\mathbf{k}\cdot\mathbf{x}(l)}n_x(1-e^{-\pi ia_0\mathbf{k}\cdot\mathbf{n}})\}^4 \tag{5.4}$$
$$=\frac{N^4}{\mu_2{}^4}\sum_{\mathbf{l}}\sum_{\mathrm{n,n.n.}}\{n_x[\Delta(\mathbf{l})-\Delta(\mathbf{l}-\mathbf{n})]\}^4. \tag{5.5}$$

Equation (5.4) is obtained from Eq. (5.3) by use of the closure relations satisfied by the eigenvectors. In obtaining Eq. (5.5) we have used the result that

$$\textstyle\sum_{\mathbf{k}}e^{2\pi i\mathbf{k}\cdot\mathbf{x}(l)}=\sum_{\mathbf{k}}e^{\pi ia_0\mathbf{k}\cdot\mathbf{l}}=N\Delta(\mathbf{l}), \tag{5.6}$$

where $\mathbf{l}$ is a dimensionless vector with integer components which is defined by

$$\mathbf{x}(l)=\tfrac{1}{2}a_0\mathbf{l}. \tag{5.7}$$

Expanding Eq. (5.5) we obtain

$$A=\frac{N^4}{\mu_2{}^4}\sum_{\mathbf{l}}\sum_{\mathrm{n,n.n.}}n_x{}^4[\Delta^4(\mathbf{l})-4\Delta^3(\mathbf{l})\Delta(\mathbf{l}-\mathbf{n})$$
$$+6\Delta^2(\mathbf{l})\Delta^2(\mathbf{l}-\mathbf{n})-4\Delta(\mathbf{l})\Delta^3(\mathbf{l}-\mathbf{n})+\Delta^4(\mathbf{l}-\mathbf{n})] \tag{5.8}$$
$$=(N^4/\mu_2{}^4)(8-4\cdot0+6\cdot0-4\cdot0+8)$$
$$=16N^4/\mu_2{}^4,$$

where the vanishing of the second, third, and fourth sums is due to the fact that $\mathbf{n}$ is restricted to be a nearest-neighbor vector.

The remaining sums are evaluated in the same way and we obtain the following results:

$$B=8N^4/\mu_2{}^4, \tag{5.9}$$
$$C=64N^5/\mu_2{}^5, \tag{5.10}$$
$$D=32N^5/\mu_2{}^5=E. \tag{5.11}$$

From Eqs. (3.23), (5.8), and (5.9) we obtain for $2M_3$ the result

$$3M_3=\frac{(kT)^3}{6M^4}\frac{\phi^{\mathrm{iv}}(r_0)}{\mu_2{}^4}[(\kappa_x{}^4+\kappa_y{}^4+\kappa_z{}^4)$$
$$+3(\kappa_x{}^2\kappa_y{}^2+\kappa_y{}^2\kappa_z{}^2+\kappa_z{}^2\kappa_x{}^2)] \tag{5.12}$$
$$=\frac{(kT)^3}{3072}\frac{\phi^{\mathrm{iv}}(r_0)}{[\phi''(r_0)]^4}[3\kappa^4-(\kappa_x{}^4+\kappa_y{}^4+\kappa_z{}^4)].$$

Similarly, from Eqs. (3.25), (5.10), and (5.11) we find that

$$-2M_4=\frac{(kT)^3}{2M^5}\frac{[\phi'''(r_0)]^2}{\mu_2{}^5}[(\kappa_x{}^4+\kappa_y{}^4+\kappa_z{}^4)$$
$$+3(\kappa_x{}^2\kappa_y{}^2+\kappa_y{}^2\kappa_z{}^2+\kappa_z{}^2\kappa_x{}^2)] \tag{5.13}$$
$$=\frac{(kT)^3}{4096}\frac{[\phi'''(r_0)]^2}{[\phi''(r_0)]^5}[3\kappa^4-(\kappa_x{}^4+\kappa_y{}^4+\kappa_z{}^4)].$$

Equations (5.12) and (5.13) clearly display the departure from isotropy in the components of $\boldsymbol{\kappa}$ of the Debye-Waller factor for cubic crystals.

The results obtained by the use of Ludwig's approximation generally underestimate the correct results, but in all cases studied so far[12,17] where the exact and approximate results can be compared the error is no more than 31%.

## VI. NUMERICAL RESULTS

Since we chose to evaluate $2M_3$ and $2M_4$ using Ludwig's approximation, the only heavy numerical calculation that had to be performed was that of $2M_2$.

The evaluation of the triple sum over $\mathbf{k}$ space which appears in Eq. (3.20),

$$S=\sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}\sum_{j_1j_2j_3}\frac{\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)F^2(\mathbf{k}_1j_1;\,\mathbf{k}_2j_2;\,\mathbf{k}_3j_3)}{\lambda^2(\mathbf{k}_1j_1)\lambda^2(\mathbf{k}_2j_2)\lambda^4(\mathbf{k}_3j_3)}, \tag{6.1}$$

was carried out numerically on an IBM 7090 computer. This sum is related to one previously evaluated for the cubic anharmonic contribution to the high-temperature free energy.[12] Unfortunately, the technique used for that problem, introduction of a Fourier series representation for the $\Delta$ function and factorization of the sums over the wave vector, which reduced the problem to a single sum over $\mathbf{k}$ space, is not applicable here because of the more complicated denominator. Certain

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[16] W. Ludwig, J. Phys. Chem. Solids 4, 2831 (1958).

[17] A. A. Maradudin and P. A. Flinn, Phys. Rev. 126, 2059 (1962).

simplifications, however, can be made. First we note that for given values of $\mathbf{k}_1$ and $\mathbf{k}_2$ the delta function condition defines a unique $\mathbf{k}_3$ in the Brillouin zone, unless $\mathbf{k}_3$ falls on a zone boundary. This may readily be seen. Consider the quantity $-(\mathbf{k}_1+\mathbf{k}_2)$; if it lies within the zone it must equal $\mathbf{k}_3$; any translation by a reciprocal lattice vector carries the point outside the zone. Similarly, if $-(\mathbf{k}_1+\mathbf{k}_2)$ lies outside the zone, a translation by some reciprocal lattice vector will carry the point to a uniquely defined $\mathbf{k}_3$ inside. The triple sum over $\mathbf{k}_1$, $\mathbf{k}_2$, and $\mathbf{k}_3$ then reduces to a double sum over $\mathbf{k}_1$ and $\mathbf{k}_2$, with $\mathbf{k}_3$ determined by the condition:

$$\mathbf{k}_3=-(\mathbf{k}_1+\mathbf{k}_2)+\boldsymbol{\tau}, \tag{6.2}$$

where $\boldsymbol{\tau}$ is the appropriate reciprocal lattice vector (possibly zero) such that $\mathbf{k}_3$ lies inside the zone. The difficulty which arises when $\mathbf{k}_3$ lies on a zone boundary and hence is not uniquely determined, is discussed below.

In addition, it is convenient to rewrite the sum in symmetrized form, so that we may make full use of the cubic symmetry in the problem. We now have to evaluate the double sum:

$$S=\sum_{\mathbf{k}_1\mathbf{k}_2}\sum_{j_1j_2j_3}\frac{F^2(\mathbf{k}_1j_1;\mathbf{k}_2j_2;\mathbf{k}_3j_3)}{\lambda^2(\mathbf{k}_1j_1)\lambda^2(\mathbf{k}_2j_2)\lambda^2(\mathbf{k}_3j_3)} \times\frac{\lambda^2(\mathbf{k}_1j_1)\lambda^2(\mathbf{k}_2j_2)+\lambda^2(\mathbf{k}_2j_2)\lambda^2(\mathbf{k}_3j_3)+\lambda^2(\mathbf{k}_3j_3)\lambda^2(\mathbf{k}_1j_1)}{3\lambda^2(\mathbf{k}_1j_1)\lambda^2(\mathbf{k}_2j_2)\lambda^2(\mathbf{k}_3j_3)}. \tag{6.3}$$

If we consider the function of $\mathbf{k}_2$ which we are left with after carrying out the sum over $\mathbf{k}_1$, it has cubic symmetry in $\mathbf{k}_2$; consequently only one sum need be evaluated over the entire zone, and the other can be restricted to the fundamental element—1/48 of the entire zone.

For the actual numerical calculation it is necessary to choose some suitable grid of points in $\mathbf{k}$ space. For our previous calculations of this sort we used a set of points of the form

$$k_x=\pm n/Na_0,\quad n=1,3,5,\cdots,N-1. \tag{6.4}$$

Such a set of points leads to certain simplifications by eliminating boundary points. This method could not be used here, however, since with $\mathbf{k}_1$ and $\mathbf{k}_2$ of odd type, $\mathbf{k}_3$ would be of even type. For this calculation, therefore, both even and odd points were used, with the attendant complication of the proper weighting for points lying on the zone boundaries. Terms in the sum corresponding to boundary points of $\mathbf{k}_1$ and $\mathbf{k}_2$ were given appropriately reduced weights. For values of $\mathbf{k}_3$ lying in the boundary only one of the equivalent points was generated and the associated term was given full weight, since the terms associated with the equivalent points would necessarily be equal, and the number of equivalent points is the same as the denominator of the weighting factor.

The calculation was carried out in the machine in two stages. In the first step, for each of the grid points in the fundamental element of the zone the elements of the dynamical matrix were evaluated with the aid of the results of Appendix A of reference 12, and the matrix was diagonalized by the Jacobi procedure, yielding its eigenvalues and eigenvectors. These were stored for use in the calculation proper. Although calculated only for the elementary 1/48 of the zone, the eigenvalues and eigenvectors were available for the entire zone, since the lookup routine incorporated the necessary symmetry operations which transform the eigenvectors corresponding to equivalent points in the zone. The calculation then proceeded by a systematic double scan of the points of the mesh in $\mathbf{k}$ space, evaluation of $\mathbf{k}_3$ for each pair of points according to Eq. (6.2), calculation of the summand, and summation.

In calculations of this complexity it is virtually essential to check the over-all correctness of the program by computing, along with the quantity of interest, one or more check quantities, as similar in form as possible, but accurately known in advance. These quantities also provide some estimate of the error associated with mesh size. For this calculation two such quantities were available from previous work. First, if we set all the $\lambda$'s in Eq. (6.3) equal to unity, we have:

$$S_a=\sum_{\mathbf{k}_1\mathbf{k}_2}\sum_{j_1j_2j_3}F^2(\mathbf{k}_1j_1;\mathbf{k}_2j_2;\mathbf{k}_3j_3). \tag{6.5}$$

This quantity was previously evaluated exactly in closed form. In addition, the sum obtained by setting the $\lambda$'s in the second factor of the summand in Eq. (6.3) equal to unity is

$$S_b=\sum_{\mathbf{k}_1\mathbf{k}_2}\sum_{j_1j_2j_3}\frac{F^2(\mathbf{k}_1j_1;\mathbf{k}_2j_2;\mathbf{k}_3j_3)}{\lambda^2(\mathbf{k}_1j_1)\lambda^2(\mathbf{k}_2j_2)\lambda^2(\mathbf{k}_3j_3)}, \tag{6.6}$$

and this is the sum required for the cubic anharmonic contribution to the high-temperature free energy. This we previously evaluated numerically by a different method.[12] The results we obtained for the three sums, and the corresponding results from our previous work are

$$S=N^2(2.027), \tag{6.7}$$

$$S_a(\text{exact})=N^2(18), \tag{6.8a}$$

$$S_a(\text{calc.})=N^2(17.99195), \tag{6.8b}$$

$$S_b(\text{present method})=N^2(2.646), \tag{6.9a}$$

$$S_b(\text{method of reference 12})=N^2(2.692). \tag{6.9b}$$

These results were obtained with a grid of 256 points in the Brillouin zone.

The agreement between the two results shown in Eq. (6.8) indicates that the present summation techniques are capable of achieving good accuracy. The good agreement between the two results shown in

Eq. (6.9) provides an independent check on the method of summation employed in reference 12 and at the same time lends support to the correctness of the result given by Eq. (6.7).

Combining Eqs. (3.20) and (6.7) we obtain finally

$$2M_2=\frac{\kappa^2}{48}(kT)^2\frac{[\phi'''(r_0)]^2}{[\phi''(r_0)]^4}(2.027). \tag{6.10}$$

We can now assemble the results of Secs. III, IV, V, and the present section, to write the following expression for $2M$ for the present model of a face-centered cubic crystal:

$$\begin{aligned}2M=&0.4191\kappa^2\frac{kT}{\phi''(\bar{r}_0)}+0.1048\kappa^2(kT)^2\frac{[\phi'''(\bar{r}_0)]^2}{[\phi''(\bar{r}_0)]^4}\\&-\kappa^2(kT)^2\frac{\phi^{\text{iv}}(\bar{r}_0)}{[\phi''(\bar{r}_0)]^3}(0.1048)+\kappa^2(kT)^2\frac{[\phi'''(\bar{r}_0)]^2}{[\phi''(\bar{r}_0)]^4}\\&\times(0.04223)+[3\kappa^4-(\kappa_x{}^4+\kappa_y{}^4+\kappa_z{}^4)](kT)^3\\&\times\left[\frac{1}{3072}\frac{\phi^{\text{iv}}(\bar{r}_0)}{[\phi''(\bar{r}_0)]^4}-\frac{1}{4096}\frac{[\phi'''(\bar{r}_0)]^2}{[\phi''(\bar{r}_0)]^5}\right]+o(\lambda^2).\end{aligned} \tag{6.11}$$

In conformity with our discussion in Sec. IV, all of the derivatives of $\phi(r)$ which appear in this expression are evaluated in the configuration which corresponds to the minimum of the potential energy.

In order to obtain an estimate of the magnitude of the anharmonic contributions to $2M$ we decided to use our model to approximate lead. The choice of lead was motivated by the fact that due to its low Debye characteristic temperature (105°K at 4.2°K[18]) even room temperature is a high temperature for lead, so that our theoretical results should apply in a temperature range where it is comparatively easy to carry out experimental measurements of the Debye-Waller factor. The shortcomings of our present model as a representation for lead have been discussed in reference 12, and we will not discuss them again here. We feel, however, that the numerical results we obtain in this way can be regarded as being indicative of the state of affairs for lead, but should not be accepted unreservedly.

The values of the various derivatives of the interatomic potential which appear in these expressions were obtained in the following way. We have seen (Eq. 4.8) that in the high temperature limit the linear expansivity is given by

$$\epsilon=\frac{kT}{4\bar{r}_0}\frac{\phi'''(\bar{r}_0)}{[\phi''(\bar{r}_0)]^2}, \tag{6.12}$$

where $\bar{r}_0$ is the value of the nearest-neighbor separation which corresponds to the minimum of the potential energy. The relation between the observed nearest-neighbor separation at temperature $T$, $r_0$, and $\bar{r}_0$ is thus given by

$$r_0=\bar{r}_0-\frac{kT}{4}\frac{\phi'''(\bar{r}_0)}{[\phi''(\bar{r}_0)]^2}. \tag{6.13}$$

From this result we see that if we take the nearest-neighbor separation at high temperatures where its dependence on temperature is linear, and extrapolate the linear behavior to the absolute zero of temperature, we obtain $\bar{r}_0$.

Similarly, Ludwig[16] and Leibfried and Ludwig[19] have pointed out that if one takes the high temperature values of the elastic constants of a solid in the region where their dependence on temperature is linear and extrapolates the linear behavior back to the absolute zero of temperature, the values of the zero temperature elastic constants so obtained are those which would be obtained in the strict harmonic approximation, i.e., from the potential energy alone. They have performed this extrapolation for many solids. This is a convenient result to use in determining numerical values for the derivatives of the interatomic potential since the expressions for the elastic constants in the harmonic approximation are particularly simple for the present model:

$$\bar{C}_{11}=(\sqrt{2}/\bar{r}_0)\phi''(\bar{r}_0),\quad \bar{C}_{12}=\bar{C}_{44}=(1/\sqrt{2}\bar{r}_0)\phi''(\bar{r}_0). \tag{6.14}$$

However, these expressions imply certain relations among the harmonic approximation elastic constants which are not satisfied by the experimental values quoted by Leibfried and Ludwig for lead:

$$\begin{aligned}\bar{C}_{11}&=5.63\times10^{11}\text{ ergs/cm}^3,\\\bar{C}_{12}&=4.59\times10^{11}\text{ ergs/cm}^3,\\\bar{C}_{44}&=1.97\times10^{11}\text{ ergs/cm}^3.\end{aligned} \tag{6.15}$$

We accordingly used the bulk modulus as a third experimental result in determining the parameters of our model since this represents an average of the elastic constants which does not explicitly display the special relations given by Eqs. (6.14). The theoretical expression for the bulk modulus in the harmonic approximation is

$$\bar{B}=\tfrac{1}{3}(\bar{C}_{11}+2\bar{C}_{12})=\frac{4}{3\sqrt{2}}\frac{1}{\bar{r}_0}\phi''(\bar{r}_0). \tag{6.16}$$

The three equations, (6.12), (6.13), and (6.16) suffice to determine the values of the three parameters $\bar{r}_0$, $\phi''(\bar{r}_0)$, and $\phi'''(\bar{r}_0)$. The values of the experimental data used in these calculations were

$$d\epsilon/dT=2.91\times10^{-5}/°\text{K}, \tag{6.17a}$$

$$r_0=3.49993\times10^{-8}\text{ cm at }273°\text{K}, \tag{6.17b}$$

$$\bar{B}=4.94\times10^{11}\text{ erg/cm}^3. \tag{6.17c}$$

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[18] D. L. Waldorf, Bull. Am. Phys. Soc. 5, 170 (1960).

[19] G. Leibfried and W. Ludwig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1961), Vol. 13, p. 275.

The value of $d\epsilon/dT$, Eq. (6.17a), was obtained from the data of Feder and Nowick[20] in a temperature range where the dependence of $\epsilon$ on $T$ is linear. The value of $r_0$ is based on unpublished work of Bolling *et al.*[21] The value of $\bar{B}$ used was obtained from the results of Leibfried and Ludwign quoted in Eq. (6.15).

The values of $\bar{r}_0$, $\phi''(\bar{r}_0)$, and $\phi'''(\bar{r}_0)$ obtained in this way are

$$\bar{r}_0=3.4723\times10^{-8}\text{ cm}, \tag{6.18a}$$

$$\phi''(\bar{r}_0)=1.8194\times10^{4}\text{ erg/cm}^2, \tag{6.18b}$$

$$\phi'''(\bar{r}_0)=-9.6929\times10^{12}\text{ erg/cm}^3. \tag{6.18c}$$

We have obtained these values without making any assumptions about the analytic form of $\phi(r)$. To obtain the fourth derivative, however, we assumed a Morse potential,

$$\phi(r)=D[(e^{-a(r-\bar{r}_0)}-1)^2-1], \tag{6.19}$$

in terms of which

$$\begin{aligned}\phi''(\bar{r}_0)&=2a^2D,\\ \phi'''(\bar{r}_0)&=-6a^3D,\\ \phi^{\text{iv}}(\bar{r}_0)&=14a^4D.\end{aligned} \tag{6.20}$$

The ratios

$$\phi'''(\bar{r}_0)/\phi''(\bar{r}_0)=-3a,\quad \phi^{\text{iv}}(\bar{r}_0)/\phi'''(\bar{r}_0)=-7a, \tag{6.21}$$

together with Eq. (6.18) suffice to determine $\phi^{\text{iv}}(\bar{r}_0)$. We obtained in this way

$$\phi^{\text{iv}}(\bar{r}_0)=4.016\times10^{21}\text{ erg/cm}^4. \tag{6.18d}$$

The values of $\phi''(\bar{r}_0)$, $\phi'''(\bar{r}_0)$, and $\phi^{\text{iv}}(\bar{r}_0)$ obtained in this way differ somewhat from the values obtained in reference 12 by a different way of fitting the experimental data. The qualitative features of the results obtained in reference 12 are, however, not affected if the present values of the potential derivatives are used instead.

Before substituting the values given by Eq. (6.18) into Eq. (6.11) we introduce two results which will simplify the form of the final answer. It is convenient to multiply and divide $\kappa$ by $a_0$, where $a_0$ is some characteristic lattice spacing. What we choose is somewhat immaterial because the result is independent of $a_0$, but we have adopted for $a_0$ the value of the lattice parameter at room temperature,[22]

$$a_0=4.9495\times10^{-8}\text{ cm}. \tag{6.22}$$

Secondly, it is convenient to introduce a characteristic temperature. We have chosen to use $\Theta_\infty$, the limiting high-temperature value of the equivalent Debye characteristic temperature, which is defined by[23]

$$\Theta_\infty=(\hbar/k)[(5/3)\mu_2]^{1/2}. \tag{6.23}$$

In Eq. (6.24) $\mu_2$ is the second moment of the frequency spectrum of the harmonic crystal. For the present model it is

$$\mu_2=4\phi''(\bar{r}_0)/M. \tag{6.24}$$

The value of $\Theta_\infty$ obtained with the results of Eq. (6.18) is

$$\Theta_\infty=143.4°\text{K}. \tag{6.25}$$

We can now rewrite Eq. (6.11) as

$$\begin{aligned}2M=(\kappa a_0)^2\frac{T}{\Theta_\infty}1.8616\times10^{-4}+(\kappa a_0)^2\left(\frac{T}{\Theta_\infty}\right)^2\\ \times[0.1438\times10^{-4}-0.1118\times10^{-4}+0.0579\times10^{-4}]\\ +a_0^4[3\kappa^4-(\kappa_x^4+\kappa_y^4+\kappa_z^4)]\left(\frac{T}{\Theta_\infty}\right)^3\\ \times[1.5428-1.4877]\times10^{-11}\end{aligned} \tag{6.26}$$

$$\begin{aligned}=(\kappa a_0)^2\left(\frac{T}{\Theta_\infty}\right)1.8616\\ \times10^{-4}\left\{1+0.0483\left(\frac{T}{\Theta_\infty}\right)\right\}.\end{aligned} \tag{6.27}$$

The order of the terms in Eq. (6.26) is the same as in Eq. (6.11).

In writing Eq. (6.27) we have omitted the anomalous contribution to $2M$. This was done because even in the most optimistic case its contribution to $2M$ for the present choice of force constants is quite negligible. We thus are led to the interesting conclusion that to a very good approximation the Debye-Waller factor for an anharmonic crystal is still given by the expression

$$e^{-2M}=\exp[-\langle(\boldsymbol{\kappa}\cdot\mathbf{u})^2\rangle], \tag{6.28}$$

where the thermal average is now to be carried out in the canonical ensemble of the anharmonic crystal. Because of the extreme complexity of the sums $2M_3$ and $2M_4$ which give rise to the anomalous terms it is difficult to estimate how general this conclusion is. However, the present result for $2M_3+2M_4$ could be increased by a factor of 15 and it would still represent no more than 10% of the contribution of the remaining anharmonic terms to $2M$ at the melting temperature of lead. Thus, assuming it were possible to increase the contribution of the anomalous terms to $2M$ by this factor, by some different way of determining the values of the derivatives of the interatomic potential, without increasing at the same time the contribution of the remaining anharmonic terms, they could still be safely neglected. Moreover, since our model was designed to reproduce several of the thermal and elastic properties of lead, it does not seem likely that another reasonable way of determining the potential parameters would lead to such a large relative increase in the contributions of $2M_3+2M_4$ as would be required to make them non-negligible.

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[20] R. Feder and A. S. Nowick, Phys. Rev. **109**, 1959 (1958).

[21] G. F. Bolling, T. B. Massalski, and C. J. McHargue (private communication).

[22] C. S. Barrett, *Structure of Metals* (McGraw-Hill Book Company, Inc., New York, 1952), p. 647.

[23] C. Domb and L. Salter, Phil. Mag. 43, 1083 (1952).

From its definition, Eq. (1.2), we see that we can express $\kappa^2$ as

$$\kappa^2=16\pi^2(\sin\theta/\lambda)^2. \tag{6.29}$$

In writing this result we have used the fact that $\cos(\mathbf{s},\mathbf{s}_0)=\cos 2\theta$, where $2\theta$ is the usual scattering angle. We can accordingly rewrite Eq. (6.27) as

$$2M=16\pi^2\left(\frac{a_0\sin\theta}{\lambda}\right)^2\left(\frac{T}{\Theta_\infty}\right)1.8616 \times 10^{-4}\left\{1+0.0483\left(\frac{T}{\Theta_\infty}\right)\right\}. \tag{6.30}$$

## VII. DISCUSSION

The numerical results for the exponent of the Debye-Waller factor obtained in the preceding section, Eqs. (6.27) or (6.30), indicate that for our model of lead the anharmonic contributions to $2M$ are of the order of 9% of its value at room temperature, and increase as we go to higher temperatures. This seems to be of a magnitude which should be readily measurable either by x-ray diffraction, elastic neutron scattering, or Mössbauer effect, experiments.

In the Debye approximation the expression for $2M$ in the high-temperature limit is given by[1]

$$2M=16\pi^2(\sin\theta/\lambda)^2 3\hbar^2 T/Mk\Theta_M{}^2, \tag{7.1}$$

where $\Theta_M$ is the so-called x-ray Debye characteristic temperature. Comparison of Eqs. (7.1) and (6.30) shows that we can express our results in the Debye form if we replace $\Theta_M$ by a temperature-dependent characteristic temperature $\Theta_M(T)$, which is given by

$$\frac{1}{\Theta_M{}^2(T)}=\frac{Mk}{\hbar^2}\frac{a_0{}^2}{\Theta_\infty}0.6205\times 10^{-4}\left\{1+0.0483\frac{T}{\Theta_\infty}\right\}. \tag{7.2}$$

This result shows that if the experimental determinations of the Debye-Waller factor at high temperatures are analyzed in terms of the Debye expression (7.1), it will be found that the x-ray Debye $\Theta$ decreases with increasing temperature. This result is opposite from the observed behavior of the specific heat Debye $\Theta$ for lead, which increases with increasing temperature.[24,12]

The general expression for $\Theta_M(T)$ obtained from Eq. (6.11) is given by

$$\frac{1}{\Theta_M{}^2(T)}=0.1397\frac{k^2}{\hbar^2}\frac{M}{\phi''(\bar{r}_0)} \times\left\{1+kT\left[0.3508\frac{[\phi'''(\bar{r}_0)]^2}{[\phi''(\bar{r}_0)]^3} -0.25\frac{\phi^{\text{iv}}(\bar{r}_0)}{[\phi''(\bar{r}_0)]^2}\right]\right\}. \tag{7.3}$$

The analysis of experimental determinations of the Debye-Waller factor with the aid of Eq. (7.3) should already provide some interesting results concerning the third and fourth derivatives of the interatomic potential in the crystal being studied. In particular, in the preceding section we have been able to estimate $\phi''(\bar{r}_0)$ and $\phi'''(\bar{r}_0)$ without making any assumptions about the analytic form of $\phi(r)$. Measurements of the temperature dependence of $2M$ together with these results and Eq. (7.3) would enable us to determine $\phi^{\text{iv}}(\bar{r}_0)$ without having to assume a Morse potential, as we have done here. At the same time, comparison of the value of $\phi^{\text{iv}}(\bar{r}_0)$ obtained experimentally in this way with the value quoted in Eq. (6.18d) would indicate how applicable a Morse potential is to lead. Eventually, through the use of more sophisticated crystal models, measurements of the Debye-Waller factor of crystals can become a very useful tool in the study of the anharmonic properties of solids.

## APPENDIX A

We derive here the result expressed by Eq. (3.12). The eigenvalue equation for the normal mode frequencies can be expressed as

$$\sum_y D_{xy}(\mathbf{k})e_y(\mathbf{k}j)=\omega^2(\mathbf{k}j)e_x(\mathbf{k}j), \tag{A1}$$

so that

$$\sum_{xy} e_x(\mathbf{k}j)D_{xy}(\mathbf{k})e_y(\mathbf{k}j)=\omega^2(\mathbf{k}j). \tag{A2}$$

The elements of the dynamical matrix for the present model are given explicitly by[12]

$$D_{xy}(\mathbf{k})=\frac{2}{M}\frac{\phi''(r_0)}{r_0{}^2}\sum_l x_0{}^l y_0{}^l \sin^2[\pi\mathbf{k}\cdot\mathbf{x}(l)], \tag{A3}$$

where the sum over $l$ runs over the twelve nearest neighbors to a given atom. Combining Eqs. (A2) and (A3) we have

$$\sum_l\sum_{xy}[x_0{}^l e_x(\mathbf{k}j)][y_0{}^l e_y(\mathbf{k}j)]\sin^2[\pi\mathbf{k}\cdot\mathbf{x}(l)] =\frac{M}{2}\frac{r_0{}^2}{\phi''(r_0)}\omega^2(\mathbf{k}j).$$

We now divide both sides of this equation by $\omega^4(\mathbf{k}j)$ and sum over $\mathbf{k}$ and $j$ to obtain

$$\sum_l\sum_{\mathbf{k}j}\sum_{xy}\frac{[x_0{}^l e_x(\mathbf{k}j)][y_0{}^l e_y(\mathbf{k}j)]}{\omega^4(\mathbf{k}j)}\sin^2[\pi\mathbf{k}\cdot\mathbf{x}(l)] =\frac{M}{2}\frac{r_0{}^2}{\phi''(r_0)}\sum_{\mathbf{k}j}\frac{1}{\omega^2(\mathbf{k}j)}. \tag{A4}$$

The sums over $\mathbf{k}$, $j$, $x$, and $y$ on the left-hand side of this equation are readily found to be independent of $l$.

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[24] G. K. Horton and H. Schiff, Proc. Roy. Soc. (London) **A250**, 248 (1959).

We thus obtain the result that

$$\sum_{\mathbf{k}j}\frac{[e_x(\mathbf{k}j)+e_y(\mathbf{k}j)]^2}{\omega^4(\mathbf{k}j)}\sin^2[\tfrac{1}{2}\pi a_0(k_x+k_y)]$$
$$=\frac{M}{12\phi''(r_0)}\sum_{\mathbf{k}j}\frac{1}{\omega^2(\mathbf{k}j)}.\quad\text{(A5)}$$

If we multiply this result by $\kappa^2 a_0^2$ we obtain Eq. (3.11).

## APPENDIX B

Since it follows simply from our analysis, we derive here the formal expression for the intensity of x rays scattered by one-phonon processes. Our starting point is Eq. (2.12) together with Eqs. (1.13), (2.21), and (2.22). What we require are those terms in the exponent of $\langle\exp\{i\boldsymbol{\kappa}\cdot[\mathbf{u}(l)-\mathbf{u}(l')]\}\rangle$ which depend on $l$ and $l$ only in the combinations $\exp\{2\pi i\mathbf{k}\cdot[\mathbf{x}(l)-\mathbf{x}(l')]\}$ and $\exp\{-2\pi i\mathbf{k}\cdot[\mathbf{x}(l)-\mathbf{x}(l')]\}$, where $\mathbf{k}$ is a typical wave vector. We make the approximation from the outset of neglecting the contributions from the anomalous terms, since if they are small in $2M$ they will be small here as well.

In the harmonic approximation the terms we require are given by the exponent of the second factor in Eq. (1.13) which we write as

$$2W_0=\frac{kT}{2NM}\sum_{\mathbf{k}j}\frac{[\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}j)]^2}{\omega^2(\mathbf{k}j)}$$
$$\times[e^{2\pi i\mathbf{k}\cdot[\mathbf{x}(l)-\mathbf{x}(l')]}+e^{-2\pi i\mathbf{k}\cdot[\mathbf{x}(l)-\mathbf{x}(l')]}].\quad\text{(B1)}$$

The desired terms arising from the term $-\beta A$ in the exponent of $\langle\exp\{i\boldsymbol{\kappa}\cdot[\mathbf{u}(l)-\mathbf{u}(l')]\}\rangle$ are obtained by multiplying out the product of $A(\mathbf{k}j)$ factors which appears in it, using Eq. (2.4). We find that the terms we want are

$$2W_1=\frac{-i}{2\beta^2N^2M^{3/2}}$$
$$\times\sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}\sum_{j_1j_2j_3}\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)\Phi(\mathbf{k}_1j_1;\,\mathbf{k}_2j_2;\,\mathbf{k}_3j_3)$$
$$\times\frac{[\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_1j_1)][\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_2j_2)][\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_3j_3)]}{\omega^2(\mathbf{k}_1j_1)\omega^2(\mathbf{k}_2j_2)\omega^2(\mathbf{k}_3j_3)}$$
$$\times[e^{2\pi i\mathbf{k}_1\cdot[\mathbf{x}(l)-\mathbf{x}(l')]}-e^{-2\pi i\mathbf{k}\cdot[\mathbf{x}(l)-\mathbf{x}(l')]}],\quad\text{(B2)}$$

where we have used the symmetry of the summand in the $\{(\mathbf{k}_ij_i)\}$ to combine terms.

In a similar way we find that the terms of the form which we require which come from $-\beta\Delta F$ in the exponent of Eq. (2.12) are

$$2W_2=-\frac{1}{4N^2M\beta^2}$$
$$\times\sum_{\mathbf{k}_1\mathbf{k}_2}\sum_{j_1j_2j_3}\frac{\Phi(\mathbf{k}_1j_1;\,-\mathbf{k}_1j_1;\,\mathbf{k}_2j_2;\,-\mathbf{k}_2j_3)}{\omega^2(\mathbf{k}_1j_1)\omega^2(\mathbf{k}_2j_2)\omega^2(\mathbf{k}_2j_3)}$$
$$\times[\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_2j_2)][\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_2j_3)]$$
$$\times[e^{2\pi i\mathbf{k}_2\cdot[\mathbf{x}(l)-\mathbf{x}(l')]}+e^{-2\pi i\mathbf{k}_2\cdot[\mathbf{x}(l)-\mathbf{x}(l')]}]$$
$$+\frac{1}{4N^2M\beta^2}\sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}\sum_{j_1j_2j_3j_4}\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)$$
$$\times\Phi(\mathbf{k}_1j_1;\,\mathbf{k}_2j_2;\,\mathbf{k}_3j_3)\Phi(-\mathbf{k}_1j_1;\,-\mathbf{k}_2j_2;\,-\mathbf{k}_3j_4)$$
$$\times\frac{[\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_3j_3)][\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_3j_4)]}{\omega^2(\mathbf{k}_1j_1)\omega^2(\mathbf{k}_2j_2)\omega^2(\mathbf{k}_3j_3)\omega^2(\mathbf{k}_3j_4)}$$
$$\times[e^{2\pi i\mathbf{k}_3\cdot[\mathbf{x}(l)-\mathbf{x}(l')]}-e^{-2\pi i\mathbf{k}_3\cdot[\mathbf{x}(l)-\mathbf{x}(l')]}].\quad\text{(B3)}$$

If we combine the results of this Appendix with those of the text, we find that the thermal average of $I$ given by Eq. (1.1) can be expressed as

$$\langle I\rangle=e^{-2M}\sum_{ll'}\exp\{i\boldsymbol{\kappa}\cdot[\mathbf{x}(l)-\mathbf{x}(l')]\}e^{2W}.\quad\text{(B4)}$$

If we expand $e^{2W}$ in powers of $2W$, the contribution to $\langle I\rangle$ from the term containing $(1/n!)(2W)^n$ is proportional to the intensity of x rays scattered by an $n$-phonon process where the terminology indicates that the wave describing the x rays couples directly to $n$ phonons of the harmonic crystal. Since we are interested in the intensity due to one-phonon processes we break off the expansion of $e^{2W}$ after the second term with the result that

$$\langle I\rangle=e^{-2M}\sum_{ll'}\exp\{i\boldsymbol{\kappa}\cdot[\mathbf{x}(l)-\mathbf{x}(l')]\}[1+2W+\cdots]$$
$$=N^2e^{-2M}\Delta(\mathbf{k})+e^{-2M}\sum_{ll'}e^{2\pi i\mathbf{k}\cdot[\mathbf{x}(l)-\mathbf{x}(l')]}2W+\cdots\quad\text{(B5)}$$
$$=I_0+I_1+\cdots.\quad\text{(B6)}$$

The first term in this expansion is just the Laue interference function modified by the effects of the thermal vibrations. The second term gives the contribution to the scattered intensity from the one-phonon processes. For convenience we have expressed the scattering vector $\boldsymbol{\kappa}$ in these expressions by

$$\boldsymbol{\kappa}=2\pi\mathbf{k}.\quad\text{(B7)}$$

The expression for $I_1$ becomes

$$I_1=e^{-2M}N^2\bigg\{\frac{kT}{2NM}\sum_{\mathbf{k}_1j}\frac{[\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_1j)]^2}{\omega^2(\mathbf{k}_1j)}[\Delta(\mathbf{k}_1+\mathbf{k})+\Delta(\mathbf{k}_1-\mathbf{k})]-i\frac{(kT)^2}{2N^2M^{3/2}}\sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}\sum_{j_1j_2j_3}\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)\Phi(\mathbf{k}_1j_1;\,\mathbf{k}_2j_2;\,\mathbf{k}_3j_3)$$
$$\times\frac{[\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_1j_1)][\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_2j_2)][\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_3j_3)]}{\omega^2(\mathbf{k}_1j_1)\omega^2(\mathbf{k}_2j_2)\omega^2(\mathbf{k}_3j_3)}[\Delta(\mathbf{k}_1+\mathbf{k})-\Delta(\mathbf{k}_1-\mathbf{k})]-\frac{(kT)^2}{4N^2M}\sum_{\mathbf{k}_1\mathbf{k}_2}\sum_{j_1j_2j_3}\frac{\Phi(\mathbf{k}_1j_1;\,-\mathbf{k}_1j_1;\,\mathbf{k}_2j_2;\,-\mathbf{k}_2j_3)}{\omega^2(\mathbf{k}_1j_1)\omega^2(\mathbf{k}_2j_2)\omega^2(\mathbf{k}_2j_3)}$$

$$\times[\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_2j_2)][\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_2j_3)][\Delta(\mathbf{k}+\mathbf{k}_2)+\Delta(\mathbf{k}-\mathbf{k}_2)]+\frac{(kT)^2}{4N^2M}\sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}\sum_{j_1j_2j_3j_4}\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)\Phi(\mathbf{k}_1j_1;\,\mathbf{k}_2j_2;\,\mathbf{k}_3j_3)$$

$$\left.\times\Phi(-\mathbf{k}_1j_1;\,-\mathbf{k}_2j_2;\,-\mathbf{k}_3j_4)\frac{[\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_3j_3)][\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_3j_4)]}{\omega^2(\mathbf{k}_1j_1)\omega^2(\mathbf{k}_2j_2)\omega^2(\mathbf{k}_3j_3)\omega^2(\mathbf{k}_3j_4)}[\Delta(\mathbf{k}+\mathbf{k}_3)+\Delta(\mathbf{k}-\mathbf{k}_3)]\right\}. \qquad \text{(B8)}$$

It should be remarked that for Bravais crystals the coefficient $\Phi(\mathbf{k}_1j_1;\,\mathbf{k}_2j_2;\,\mathbf{k}_3j_3)$ is purely imaginary. This result follows from the fact that

$$\Phi(\mathbf{k}_1j_1;\,\mathbf{k}_2j_2;\,\mathbf{k}_3j_3)=\Phi^*(-\mathbf{k}_1j_1;\,-\mathbf{k}_2j_2;\,-\mathbf{k}_3j_3),$$

together with the result that

$$\Phi(-\mathbf{k}_1j_1;\,-\mathbf{k}_2j_2;\,-\mathbf{k}_3j_3)=-\Phi(\mathbf{k}_1j_1;\,\mathbf{k}_2j_2;\,\mathbf{k}_3j_3),$$

which is a consequence of the transformation properties of the third-order atomic force constants under the inversion operation. This means that the second term in Eq. (B8) is real, as it must be.

Although the result given by Eq. (B8) looks cumbersome, its evaluation as a function of **k** for a simple model of a crystal does not appear to be out of the question. A correction for thermal expansion can also be applied to the first term of this result, but we have not done so here.