[†] Research supported in part by the Advanced Research Projects Agency under Contract No. SD-131.

[1] W. H. Adams, J. Chem. Phys. 34, 89 (1961); 37, 2009 (1962).

[2] T. L. Gilbert, in *Molecular Orbitals in Chemistry, Physics, and Biology*, edited by P. O. Löwdin and B. Pullman (Academic, New York, 1964).

[3] P. W. Anderson, Phys. Rev. Letters 21, 13 (1968).

[4] A. B. Kunz, Phys. Status Solidi 36, 301 (1969).

[5] D. W. Hafemeister and W. H. Flygare, J. Chem. Phys. 43, 795 (1965).

[6] C. C. J. Roothaan, Rev. Mod. Phys. 23, 69 (1951); 32, 179 (1960).

[7] A. B. Kunz, J. Phys. C 3, 1542 (1970).

[8] A. B. Kunz, Bull. Am. Phys. Soc. 15, 369 (1960), Abstract No. KF11.

[9] P. S. Bagus, Phys. Rev. 139, A619 (1965).

[10] R. E. Watson and A. J. Freeman, Phys. Rev. 123, 521 (1961).

[11] R. E. Watson and A. J. Freeman, Phys. Rev. 124, 1117 (1961).

[12] D. R. Hartree, *The Calculations of Atomic Structures* (Wiley, New York, 1957).

[13] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) A156, 45, (1936).

[14] N. O. Lipari (unpublished).

[15] W. B. Fowler and A. B. Kunz, Phys. Status Solidi (to be published).

PHYSICAL REVIEW B VOLUME 2, NUMBER 6 15 SEPTEMBER 1970

Thermal Expansion and Phonon Frequency Shifts in Nonprimitive Lattices

E. Leo Slaggie
Gulf General Atomic Incorporated, San Diego, California 92112

(Received 30 January 1970)

Expressions have been derived in the quasiharmonic approximation for the change in normal-mode frequencies associated with thermal expansion in a nonprimitive lattice. The work is formulated in terms of coupling parameters for an undistorted lattice with cubic anharmonicity. Symmetric finite-strain parameters and appropriate internal strains are introduced in such a manner that the formulation exhibits explicitly the invariance of the crystal potential energy and normal-mode frequencies under rigid-body rotations. As a numerical application, the coefficient of linear expansion and the phonon frequency distributions at 300 and 800 °K have been calculated for zirconium hydride with a short-range central-force model including third-nearest-neighbor forces.

I. INTRODUCTION

The temperature dependence of phonon frequencies in a crystal can be conveniently divided into two parts: (1) a quasiharmonic part associated with thermal expansion, which results in a change of interatomic distances and a corresponding change in the harmonic force constants, and (2) a part arising directly from terms in the potential-energy expansion of higher order than quadratic in powers of displacements of the atoms from their mean positions. We shall refer to the latter contribution, which is present even if the crystal is held at constant volume, as a pure anharmonic effect. In this paper we are concerned with the effects of thermal expansion on phonon frequencies. This problem was considered in a plausible but nonrigorous manner by Maradudin and Fein[1] as part of a study of anharmonic effects on neutron scattering by Bravais crystals. Further justification for their result was later provided by Maradudin[2] in a separate study also limited to Bravais crystals, in which explicit expressions for thermal deformations and frequency shifts in terms of force constants were given. Neutron scattering and thermal expansion in more general anharmonic crystals have been studied by Cowley.[3] However, in these treatments the introduction of finite-strain parameters[4] was carried out in an approximate manner and internal strains (relative displacement of sublattices) were not included. It turns out that it is possible to introduce finite-strain parameters rigorously, so that at all stages of the calculation the phonon frequencies are manifestly invariant under rigid-body rotation of the crystal (in the absence of external forces or fields). Constructing the formalism in this manner is not only desirable from the standpoint of elegance but is also essential in the event that an extension to higher orders of approximation becomes necessary – for example, over wide temperature ranges for a strongly anharmonic crystal.

It is the purpose of the present paper to study thermal expansion and related phonon frequency shifts in nonprimitive lattices, employing a rigorous introduction of finite-strain parameters and appropriate internal strains. The calculation follows Maradudin's work[2] in broad outline but incorporates many changes and additions associated with the more general problems presented by nonprimitive crystals. In the special case of primitive lattices we confirm Maradudin's results. We use the formalism of general lattice-dynamical theory as found in the book by Born and Huang[4] and elaborated by Leibfried and Ludwig[5] for the case of anharmonic crystals. Expressions are given for the potential energy, phonon frequencies, and free energy of a lattice distorted from a configuration in which the potential energy is minimized. These expressions involve coupling parameters defined with respect to the undistorted lattice and parameters which characterize the distortion. The temperature-dependent finite-strain parameters which minimize the free energy are then expressed in terms of the coupling parameters for the undistorted lattice. Although the quasiharmonic approximation[5] is used here, a generalization to higher orders of approximation appears straightforward. Since long-range Coulomb effects are not considered, the application of the work is limited to nonpiezoelectric crystals.

Part of the incentive for this work has been the desire to extend the scope of anharmonic calculations to a wider range of solids, including some important reactor moderators. Therefore, we have chosen as a numerical example to calculate the thermal expansion and associated phonon frequency shifts for zirconium hydride a moderator for which a fairly elaborate harmonic central-force model is already in existence.[6] Phonon frequency distributions obtained from this model and from similar models for other moderators are used extensively in the description of neutron thermalization in solids.[7] However, such models must be parametrized to fit a set of data taken at a particular temperature (usually room temperature) and can be used in thermalization problems at other temperatures only under the assumption that the frequency spectrum does not change significantly. Since sufficient data at diverse temperatures to check this assumption are not yet avaliable, there is a need for theoretical work incorporating anharmonic effects, even on a very phenomenological basis, to study the temperature dependence of frequency distributions used in thermalization calculations. We present in Sec. V frequency distributions for zirconium hydride at 300 and 800 °K calculated from an anharmonic central-force model that predicts a coefficient of linear expansion in satisfactory agreement with the measured value. The temperature dependence seen in the calculated results is large enough to show up in neutron scattering experiments, though it will probably not affect thermalization calculations significantly. These conclusions are tentative, however, since the shifts associated with purely anharmonic effects have not been calculated. Previous calculations[1,3] indicate that their net contribution is probably significantly smaller than the thermal-expansion shifts.

II. EXPANSION OF POTENTIAL IN TERMS OF DISTORTION PARAMETERS

We first expand the potential energy Φ of a crystal in powers of displacements from the configuration in which the potential energy is a minimum (when summation indices are suppressed, summation over repeated indices is implied except when the contex indicates otherwise):

$$\Phi = \tilde{\Phi}_0 + \sum_{n=2}^{\infty} \frac{1}{n!} \sum \tilde{\Phi}_{\alpha_1 \cdots \alpha_n}(l_1 k_1; \cdots l_n k_n) \prod_{i=1}^{n} \epsilon_{\alpha_i}(l_i k_i). \tag{2. 1}$$

In (2. 1), $\tilde{\Phi}_0$ is a constant term; $\epsilon_\alpha(l k)$ denotes the α component of the displacement of the kth atom in the lth unit cell from the rest position, to be denoted below as $\vec{X}(l k)$ in the notation of Born and Huang.[4] The coupling parameters (CP) $\Phi_{\alpha_1 \cdots \alpha_n}(l_1 k_1; \cdots l_n k_n)$, are defined as

$$\tilde{\Phi}_{\alpha_1 \cdots \alpha_n}(l_1 k_1; \cdots l_n k_n) \equiv \left(\frac{\partial^n \Phi}{\partial \epsilon_{\alpha_1}(l_1 k_1) \cdots \partial \epsilon_{\alpha_n}(l_n k_n)} \right)_0 , \tag{2. 2}$$

where the bracket indicates that the partial derivatives are to be evaluated at $\epsilon_\alpha(l k) = 0$. From the condition that the potential energy is a minimum in the undistorted lattice we have

$$\tilde{\Phi}_\alpha(l k) \equiv 0. \tag{2. 3}$$

The CP's defined by (2. 2) are clearly invariant under the permutation

$$\alpha_i, l_i, k_i \leftrightarrow \alpha_j, l_j, k_j .$$

For definiteness we assume the crystal to contain N unit cells ($N \gg 1$), each containing r atoms, and we assume periodic boundary conditions. Thus in (2. 1) and following equations a summation over l indicates a summation over N triplets of cell indices specifying the unit-cell positions. Summations over k are from 1 to r, while Greek subscripts are summed from 1 to 3.

Next, we consider the displacement $\epsilon_\alpha(l k)$ to consist of three parts, as follows:

$$\epsilon_\alpha(l k) = \sum_\beta \epsilon_{\alpha\beta} X_\beta(l k) + d_\alpha(k) + u_\alpha(l k). \tag{2. 4}$$

The first two terms of (2. 4) describe, respectively, a homogeneous deformation of the crystal from the rest configuration, the parameters $\epsilon_{\alpha\beta}$ being constants describing the deformation, followed by a further static displacement $d_\alpha(k)$ of the kth atom in each cell such that a new distorted lattice is formed with atoms $(l k)$ at positions with coordinates $X'_\alpha(l k)$ given by the expression

$$X'_\alpha(l k) = X_\alpha(l k) + \sum_\beta \epsilon_{\alpha\beta} X_\beta(l k) + d_\alpha(k). \tag{2.5}$$

The displacement $d_\alpha(k)$ corresponds to a rigid static displacement of the sublattices. Finally, $u_\alpha(l k)$ denotes a dynamic displacement of atom (lk) from its position in the distorted lattice. (For simplicity of notation we do not indicate the time dependence explicitly.) Since we are interpreting the terms $X'_\alpha(l k)$ of (2.5) as position-vector components describing a distorted lattice, i.e., an array of mean positions about which the atoms execute thermal motions, it is consistent to require the dynamic displacements to satisfy the condition

$$\langle u_\alpha(l k)\rangle = 0, \tag{2.6}$$

where the brackets denote the thermodynamic expectation value. For a general operator ϕ this expectation value in the canonical ensemble for a system at temperature T with the Hamiltonian H is given by the relation

$$\langle\phi\rangle = \mathrm{Tr}(e^{-\beta H}\phi)/\mathrm{Tr}(e^{-\beta H}) = \frac{1}{Z}\sum_m \langle m | e^{-\beta H}\phi | m\rangle , \tag{2.7}$$

where $\beta = (k_B T)^{-1}$, k_B being Boltzmann's constant, Z is the partition function for the system, and the $|m\rangle$'s are an arbitrary complete orthonormal set of functions. The condition (2.6) removes the ambiguity otherwise present in a decomposition like (2.4), in which except for (2.6) an arbitrary amount of the static displacement could be formally included in $u_\alpha(l k)$.

To remove the formal dependence on crystal orientation introduced in Φ by substituting (2.4) in (2.1) it is necessary to use the symmetric finite-strain parameters $\eta_{\alpha\beta}$ defined as follows:

$$\eta_{\alpha\beta} = \tfrac{1}{2}\left(\epsilon_{\alpha\beta} + \epsilon_{\beta\alpha} + \sum_\gamma \epsilon_{\gamma\alpha}\epsilon_{\gamma\beta}\right). \tag{2.8}$$

In a lattice subjected to an external strain such that the lattice points are displaced by an amount given by the first term on the right-hand side of (2.4), the separation between any two lattice points is determined by the parameters $\eta_{\alpha\beta}$.[4] As an illustration, we observe that a rigid rotation of the crystal is described by a set of parameters $\epsilon_{\alpha\beta}$ such that the terms $\delta_{\alpha\beta} + \epsilon_{\alpha\beta}$ are the components of an orthogonal matrix, i.e.,

$$\sum_{\beta'} (\delta_{\alpha\beta'} + \epsilon_{\beta'\alpha})(\delta_{\beta'\beta} + \epsilon_{\beta'\beta}) = \delta_{\alpha\beta} .$$

We obtain for such an $\epsilon_{\alpha\beta}$ using (2.8) the result $\eta_{\alpha\beta} = 0$. Thus, a rigid rotation is clearly equivalent to vanishing strain in a formalism expressed in terms of $\eta_{\alpha\beta}$.

Since the static and dynamic displacements represented, respectively, by $d_\alpha(k)$ and $u_\alpha(l k)$ are referred to a particular orientation of the crystal, the orientation-independent representation of a general strain requires in conjunction with $\eta_{\alpha\beta}$ the use of the parameters $\bar{d}_\alpha(k)$ and $\bar{u}_\alpha(l k)$ given as follows[4]:

$$\bar{d}_\alpha(l k) = d_\alpha(k) + \sum_\beta \epsilon_{\beta\alpha} d_\beta(k), \tag{2.9a}$$

$$\bar{u}_\alpha(l k) = u_\alpha(l k) + \sum_\beta \epsilon_{\beta\alpha} u_\beta(l k). \tag{2.9b}$$

For a given $\epsilon_{\alpha\beta}$ we have from (2.6) the requirement

$$\langle \bar{u}_\alpha(l k)\rangle = 0. \tag{2.9c}$$

Our goal now is to obtain an expansion for Φ in powers of $\bar{u}_\alpha(k)$ of the form

$$\Phi = \sum_{n=0}^{\infty} \frac{1}{n!} \sum \Phi_{\alpha_1 \cdots \alpha_n}(l_1 k_1; \cdots l_n k_n) \times \bar{u}_{\alpha_1}(l_1 k_1) \cdots \bar{u}_{\alpha_n}(l_n k_n), \tag{2.10}$$

in which $\Phi_{\alpha_1 \cdots \alpha_n}(l_1 k_1; \cdots l_n k_n)$ is a generalized coupling parameter pertaining to the distorted lattice. By a straightforward but tedious substitution of (2.4) in (2.1) these parameters can be found in terms of the distortion parameters $\eta_{\alpha\beta}$ and $\bar{d}_\alpha(k)$ and the CP's for the undistorted lattice. This procedure is described and explicit expressions for the coefficients are given in Gulf General Atomic reports.[8,9] These expressions are displayed where needed in the following sections.

III. NORMAL-MODE FREQUENCIES IN DISTORTED LATTICES

The basic equations of motion for an atom in the deformed crystal are

$$m_k \ddot{u}_\alpha(l k) = -\frac{\partial\Phi}{\partial u_\alpha(l k)} . \tag{3.1}$$

By use of (2.8) and (2.9b) we can rewrite these equations as

$$m_k \ddot{\bar{u}}(l k) = -\sum_{\alpha'} (\delta_{\alpha\alpha'} + 2\eta_{\alpha\alpha'}) \frac{\partial\Phi}{\partial\bar{u}_{\alpha'}(l k)} . \tag{3.2}$$

At this point we write out explicitly the first few terms of the expansion (2.10) for the potential energy:

$$\Phi = \Phi_0 + \tfrac{1}{2}\sum \Phi_{\alpha\alpha'}(l k; l' k')\, \bar{u}_\alpha(l k)\, \bar{u}_{\alpha'}(l' k')$$

$$+\left[\sum \Phi_\alpha(lk)\,\bar{u}_\alpha(lk)+\tfrac{1}{6}\sum \Phi_{\alpha\alpha'\alpha''}(lk;l'k';l''k'')\right.$$
$$\left.\times\,\bar{u}_\alpha(lk)\,\bar{u}_{\alpha'}(l'k')\bar{u}_{\alpha''}(l''k'')+\cdots\right]. \qquad (3.3)$$

The terms in (3.3) within the bracket vanish in the strict harmonic approximation. Introducing anharmonicity, for example,

$$\tilde{\Phi}_{\alpha\alpha'\alpha''}(lk;l'k';l''k'')\neq 0,$$

makes $\Phi_{\alpha\alpha'}(lk;l'k')$ dependent on the distortion parameters and also introduces nonvanishing terms into the bracket in (3.3).[9] All of these terms except the first, however, are of third or higher order in the presumably small dynamic displacements $\bar{u}_\alpha(lk)$. Hence to lowest order we can neglect the contributions made by these terms to the dependence of the potential energy on the distortion parameters. Distortion-independent contributions to neutron scattering from cubic and quartic terms in (3.3) are what we have called pure anharmonic effects. These contributions have been studied by Maradudin and Fein[1] and by Cowley.[3] We shall call the approximation of neglecting all the bracketed terms in (3.3) the "quasiharmonic approximation," in which anharmonic effects are introduced through the dependence of $\Phi_{\alpha\alpha'}(lk;l'k')$ on the distortion parameters and anharmonic CP's as given below [see (3.7)].

In this section we wish to calculate normal-mode frequencies, which are unaffected by the addition of a constant force like that which the linear term in (3.3) contributes to the equations of motion (3.2). Hence we can use the quasiharmonic approximation. Later on, when we calculate the free energy of the distorted crystal, we shall consider corrections introduced by the linear term in (3.3).

Using the permutation properties of the generalized CP's, we thus write the equations of motion in the form

$$m_k\ddot{\bar{u}}_\alpha(lk)=-\sum\nolimits_{\alpha'}(\delta_{\alpha\alpha'}+2\eta_{\alpha\alpha'})$$
$$\times\sum \Phi_{\alpha'\alpha''}(lk;l'k')\bar{u}_{\alpha''}(l'k'). \qquad (3.4)$$

By assuming running-wave solutions for $\bar{u}_\alpha(lk)$,

$$\bar{u}_\alpha(lk)=[\bar{u}_\alpha^{(0)}(k)/(m_k)^{-1/2}]\,e^{-i\omega t+2\pi i\vec{q}\cdot\vec{x}(l)}, \qquad (3.5)$$

where $x(l)$ denotes the position vector of the lth unit cell, and where $\bar{u}_\alpha^{(0)}(k)$ is time independent, we obtain from (3.4) the equation

$$\omega^2\bar{u}_\alpha^{(0)}(k)=\sum\nolimits_{\alpha'}(\delta_{\alpha\alpha'}+2\eta_{\alpha\alpha'})\sum \Phi_{\alpha'\alpha''}$$
$$\times(lk;l'k')\bar{u}_{\alpha''}^{(0)}(k')(m_k m_{k'})^{-1/2}$$
$$\times\exp\{2\pi i\vec{q}\cdot[\vec{x}(l')-\vec{x}(l)]\}. \qquad (3.6)$$

The wave vector $\vec{q}$ and position vector $\vec{x}(l)$ in (3.5) and (3.6) can be chosen conveniently as vectors appropriate to the undistorted lattice, since the product $\vec{x}(l)\cdot\vec{q}$ is invariant against homogeneous deformations.[2]

We can write the generalized CP in (3.6) in terms of the CP's and lattice coordinates referred to the undistorted lattice as follows[9]:

$$\Phi_{\alpha\alpha'}(lk;l'k')=\tilde{\Phi}_{\alpha\alpha'}(lk;l'k')+\sum\tilde{\Phi}_{\alpha\alpha'\alpha''}(lk;l'k';l''k'')\bar{d}_{\alpha''}(k'')+\sum_{\alpha''\beta''}\eta_{\alpha''\beta''}$$
$$\times\left[\sum\tilde{\Phi}_{\alpha\alpha'\alpha''}(lk;l'k';l''k'')X_{\beta''}(l''k'')-\delta_{\alpha''\alpha}\tilde{\Phi}_{\beta''\alpha'}(lk;l'k')-\delta_{\alpha''\alpha'}\tilde{\Phi}_{\beta''\alpha}(l'k';lk)\right]. \qquad (3.7)$$

As a consequence of periodicity properties and translation invariance of the lattice, the CP's satisfy the relations[5]

$$\tilde{\Phi}_{\alpha_1\cdots\alpha_n}(l_1k_1;l_2k_2;\cdots l_nk_n)$$
$$=\tilde{\Phi}_{\alpha_1\cdots\alpha_n}(0k_1;l_2-l_1,k_2;\cdots l_n-l_1,k_n), \qquad (3.8a)$$

$$\sum_{l_ik_i}\tilde{\Phi}_{\alpha_1\cdots\alpha_i\cdots\alpha_n}(l_1k_1;\cdots l_ik_i;\cdots l_nk_n)=0. \qquad (3.8b)$$

Applying (3.8) to (3.7), we can confirm directly the result that (3.8a) and (3.8b) hold when $\tilde{\Phi}_{\alpha\alpha'}(lk;l'k')$ is replaced by $\Phi_{\alpha\alpha'}(lk;l'k')$, which must be the case since a distorted lattice is still a crystal. Thus by use of property (3.8) the l dependence can be removed from the right-hand side of (3.6), which is then seen to be an eigenvalue equation for the distorted lattice of the form

$$\omega^2\bar{u}_\alpha^{(0)}(k)=\sum d_{\alpha\alpha'}(\vec{q},kk')\,\bar{u}_\alpha^{(0)}(k'), \qquad (3.9)$$

where $d_{\alpha\alpha'}(\vec{q},kk')$ denotes the dynamical matrix, given by the expression

$$d_{\alpha\alpha'}(\vec{q},kk')=(m_k m_{k'})^{-1/2}\sum\nolimits_l\left[\sum\nolimits_{\alpha'}(\delta_{\alpha\alpha''}+2\eta_{\alpha\alpha''})\right.$$
$$\left.\times\,\Phi_{\alpha''\alpha'}(0k;lk')\right]e^{2\pi i\vec{q}\cdot\vec{x}(l)}. \qquad (3.10)$$

By substituting (3. 7) into (3. 10) and dropping terms of higher than first order in $\eta_{\alpha\beta}$ and $\bar{d}_\alpha(k)$, we obtain for the dynamical matrix

$$d_{\alpha\alpha'}(\vec{q}, kk') = \tilde{d}_{\alpha\alpha'}(\vec{q}, kk') + \sum_{\alpha''\beta''} d^{(1)}_{\alpha\alpha';\alpha''\beta''} \times (\vec{q}, kk')\, \eta_{\alpha''\beta''} + \sum d^{(2)}_{\alpha\alpha'\alpha''}(\vec{q}, kk'k'')\bar{d}_{\alpha''}(k''), \qquad (3.11)$$

where

$$\tilde{d}_{\alpha\alpha'}(\vec{q}, kk') = (m_k m_{k'})^{-1/2} \sum_l \tilde{\Phi}_{\alpha\alpha'}(0k; lk')e^{2\pi i\vec{q}\cdot\vec{x}(l)}, \qquad (3.12)$$

$$d^{(1)}_{\alpha\alpha'}(\vec{q}, kk') = (m_k m_{k'})^{-1/2} \times \sum \tilde{\Phi}_{\alpha\alpha'\alpha''}(0k; lk'; l'k'')X_{\beta''}(l'k'') \times e^{2\pi i\vec{q}\cdot\vec{x}(l)} - \delta_{\alpha''\alpha'}\tilde{d}_{\alpha\beta''}(\vec{q}, kk') + \delta_{\alpha\beta''}\tilde{d}_{\alpha''\alpha'}(\vec{q}, kk'), \qquad (3.13)$$

and

$$d^{(2)}_{\alpha\alpha'\alpha''}(\vec{q}, kk'k'') = (m_k m_{k'})^{-1/2} \sum \tilde{\Phi}_{\alpha\alpha'\alpha''} \times (0k; l'k'; lk'')\, e^{2\pi i\vec{q}\cdot\vec{x}(l')}. \qquad (3.14)$$

Using (3. 12) and the rotation-invariance conditions on the CP's[10] it can be confirmed directly that $d^{(1)}_{\alpha\alpha';\alpha''\beta''}(\vec{q}, kk')$ is symmetric in α'' and β''.

For each value of $\vec{q}$ the eigenvalue equation (3. 9) for the normal-mode frequencies in the distorted lattice has $3r$ solutions, obtained from the secular equation

$$\det \| d_{\alpha\alpha'}(\vec{q}, kk') - \delta_{\alpha\alpha'}\delta_{kk'}\,\omega^2(\vec{q})\| = 0, \qquad (3.15)$$

where r is the number of atoms per unit cell. We denote these solutions by $\omega^2(\vec{q}, j)$, where $j = 1, \ldots, 3r$. Likewise the frequencies for the undistorted lattice are solutions of the secular equation

$$\det \| \tilde{d}_{\alpha\alpha'}(\vec{q}, kk') - \delta_{\alpha\alpha'}\delta_{kk'}\,\tilde{\omega}^2(\vec{q})\| = 0, \qquad (3.16)$$

which we denote by $\tilde{\omega}^2(\vec{q}, j)$, $j = 1, \ldots, 3r$. To lowest order in $\eta_{\alpha\beta}$ and $\bar{d}_\alpha(lk)$ it is easy to obtain by a perturbation calculation, using (3. 11), the result

$$\omega^2(\vec{q}, j) = \tilde{\omega}^2(\vec{q}, j) + \sum_{\alpha\alpha'} \tilde{e}^*_\alpha(\vec{q}, kj)\Big[\sum_{\alpha''\beta''} d^{(1)}_{\alpha\alpha';\alpha''\beta''} \times (\vec{q}, kk')\,\eta_{\alpha''\beta''} + \sum_{\alpha''k''} d^{(2)}_{\alpha\alpha'\alpha''} \times (\vec{q}, kk'k'')\bar{d}_{\alpha''}(k'')\Big]\,\tilde{e}_{\alpha'}(\vec{q}, k'j). \qquad (3.17)$$

In (3. 17), $\tilde{e}_\alpha(\vec{q}, kj)$ denotes the α component of the normalized eigenvector for the undistorted lattice, which satisfies the equation

$$\tilde{\omega}^2(\vec{q}, j)\,\tilde{e}_\alpha(\vec{q}, kj) = \sum \tilde{d}_{\alpha\alpha'}(\vec{q}, kk')e_{\alpha'}(\vec{q}, k'j). \qquad (3.18)$$

The harmonic terms in (3. 13) make no contribution to the right-hand side of (3. 17), as can be seen by use of (3. 18) and the Hermiticity of the dynamical matrix (see below).

Thus we can reduce (3. 17) to the form

$$\omega^2(\vec{q}, j) = \tilde{\omega}^2(\vec{q}, j) + \sum_{\alpha\beta} \eta_{\alpha\beta}\, d^{(1)}_{\alpha\beta}(\vec{q}, j) + \sum \bar{d}_\alpha(k) d^{(2)}_\alpha(\vec{q}, kj), \qquad (3.19)$$

where

$$d^{(1)}_{\alpha\beta}(\vec{q}, j) \equiv \sum \tilde{e}^*_{\alpha'}(\vec{q}, kj)\,\tilde{e}_{\alpha''}(\vec{q}, k'j)\, d_{\alpha'\alpha'';\alpha\beta}(\vec{q}, kk') \qquad (3.20)$$

with

$$d_{\alpha'\alpha'';\alpha\beta}(\vec{q}, kk') = (m_k m_{k'})^{-1/2} \sum \tilde{\Phi}_{\alpha'\alpha''\alpha} \times (0k; lk'; l'k'')X_\beta(l'k'')\, e^{2\pi i\vec{q}\cdot\vec{x}(l)}. \qquad (3.21)$$

Also,

$$d^{(2)}_\alpha(\vec{q}, kj) \equiv \sum \tilde{e}^*_{\alpha'}(\vec{q}, k'j)\,\tilde{e}_{\alpha''} \times (\vec{q}, k''j)\, d^{(2)}_{\alpha'\alpha''\alpha}(\vec{q}, k'k''k), \qquad (3.22)$$

where $d^{(2)}_{\alpha'\alpha''\alpha}(\vec{q}, k'k''k)$ is given by (3. 14). It follows by use of (3. 18) and the α'', β'' symmetry of $d^{(1)}_{\alpha\alpha';\alpha''\beta''}(\vec{q}, kk')$ that $d^{(1)}_{\alpha\beta}(\vec{q}, j)$ is symmetric in α, β. By virtue of the symmetry of $\eta_{\alpha\beta}$, an antisymmetric part of $d^{(1)}_{\alpha\beta}(\vec{q}, j)$ would not in any case contribute to the sum over α, β in (3. 19).

The dynamical matrix for the undistorted lattice is Hermitian:

$$\tilde{d}_{\alpha\alpha'}(\vec{q}, kk') = \tilde{d}_{\alpha'\alpha}(\vec{q}, k'k),$$

as can be seen from the permutation and translation invariance properties of $\tilde{\Phi}_{\alpha\alpha'}(0k; lk')$. The squared normal-mode frequencies $\tilde{\omega}^2(\vec{q}, j)$ are thus real (and must be positive for a stable lattice). Although $d_{\alpha\alpha'}(\vec{q}, kk')$ as given by (3. 10) is not itself Hermitian, because of the additional matrix multiplication by $I+2\eta$, it can be shown[9] to be similar to a Hermitian matrix so that $\tilde{\omega}^2(\vec{q},j)$ is also real.

We next use thermodynamic equilibrium conditions to find expressions for the strains $\eta_{\alpha\beta}$ and static displacements $\bar{d}_\alpha(k)$ associated with thermal expansion.

IV. DETERMINATION OF DISTORTION PARAMETERS

For a given external strain described by the parameters $\eta_{\alpha\beta}$ the associated internal strains $\bar{d}_\alpha(k)$ are determined by (2.6), the vanishing of the average dynamic displacement. In studying the consequences of this condition it is convenient to work with the Helmholtz free energy $F(\beta)$, where $\beta=(k_B T)^{-1}$. [This standard notation for $(k_B T)^{-1}$ should not cause confusion with the use elsewhere of the symbol β as a subscript.] We shall later determine $\eta_{\alpha\beta}$ by minimizing $F(\beta)$, which is related to the partition function Z by the equation

$$F(\beta)=(-1/\beta)\ln Z, \tag{4.1}$$

where

$$Z=\mathrm{Tr}(e^{-\beta H}). \tag{4.2}$$

We write the Hamiltonian of the crystal in the form

$$H=\Phi_0+H^{\mathrm{qh}}+H^A, \tag{4.3}$$

where H^{qH} denotes the quasiharmonic part of the total Hamiltonian,

$$H^{\mathrm{qh}}=T_0+\tfrac{1}{2}\sum \Phi_{\alpha\alpha'}(lk;l'k')\,\bar{u}_\alpha(lk)\,\bar{u}_{\alpha'}(l',k'), \tag{4.4}$$

T_0 being the kinetic energy of the lattice. In (4.3), Φ_0 (as distinguished from $\tilde{\Phi}_0$) represents the static part of the Hamiltonian and depends (see below) on the distortion parameters. H^A includes the anharmonic terms in the bracket of (3.3). Since we are dropping terms of order higher than quadratic in $\bar{u}_\alpha(lk)$ we can write

$$H^A=\sum \Phi_\alpha(lk)\,\bar{u}_\alpha(lk). \tag{4.5}$$

Using (4.1)–(4.5) and (2.7), we find by using the cyclic invariance of the trace the formal relation[11]

$$\langle\bar{u}(lk)\rangle=\frac{\partial F}{\partial[\Phi_\alpha(lk)]}, \tag{4.6}$$

where the partial derivation is taken by holding all distorted-lattice CP's constant except $\Phi_\alpha(lk)$. We shall use (4.6) below in conjunction with (2.9c) to relate the internal and external strains. Using (4.1) and (4.3), we note that F can be divided into a static and a dynamic part,

$$F=F_s+F_d, \tag{4.7}$$

where

$$F_s=\Phi_0 \tag{4.8}$$

and

$$F_d=-\beta^{-1}\ln\mathrm{Tr}\{\exp[-\beta(H^{\mathrm{qh}}+H^A)]\}. \tag{4.9}$$

Treating H^A as a perturbation, we can make the further decomposition

$$F_d=F^{\mathrm{qh}}+\Delta F, \tag{4.10}$$

where[5]

$$F^{\mathrm{qh}}=-\beta^{-1}\ln\mathrm{Tr}\{\exp[-\beta H^{\mathrm{qh}}]\}$$
$$=\beta^{-1}\sum_{\vec{q}j}\ln\{2\sinh[\tfrac{1}{2}\beta\hbar\omega(\vec{q},j)]\}. \tag{4.11}$$

The sum over $\vec{q}$ in (4.11) covers values restricted to the first Brillouin zone.

The anharmonic contribution ΔF can be evaluated by a perturbation expansion using formulas given by Leibfried and Ludwig[5] or, more conveniently, by a diagrammatic analysis.[3,11] To lowest order, ΔF is given by the expression

$$\Delta F=-(2N)^{-1}{\sum_j}'\frac{1}{\omega^2(\vec{0},j)}\left|\sum m_k^{-1/2}\,\Phi_\alpha(lk)\,\hat{e}_\alpha(\vec{0},kj)\right|^2, \tag{4.12}$$

where $\hat{e}_\alpha(\vec{0},kj)$ denotes a component of the normalized eigenvector of the distorted lattice-dynamical matrix given by (3.11). The prime on the summation indicates that acoustic modes are omitted. We note that since Φ_0 and F^{qh} are independent of $\Phi_\alpha(lk)$, we can write from (4.6)

$$\langle\bar{u}_\alpha(lk)\rangle=\frac{\partial\Delta F}{\partial[\Phi(lk)]}\,. \tag{4.13}$$

Condition (2.9c) then leads to the requirement

$${\sum_j}'\frac{1}{\omega^2(\vec{0},j)}\sum(m_k m_{k'})^{-1/2}$$
$$\times\,\hat{e}_\alpha(\vec{0},kj)\,\hat{e}_{\alpha'}(\vec{0},k'j)\,\Phi_{\alpha'}(lk)=0, \tag{4.14}$$

where we have used the fact for vanishing $\vec{q}$ the eigenvectors can be taken to be real. To lowest order in $\eta_{\alpha\beta}$ and $\bar{d}_\alpha(k)$ the generalized coupling parameter appearing in (4.14) has the form[9]

$$\Phi_\alpha(lk)=\sum \bar{d}_{\alpha'}(k')\,\tilde{\Phi}_{\alpha\alpha'}(lk;l'k')$$
$$+\sum_{\alpha'\beta'}\eta_{\alpha'\beta'}\sum_{l'k'}\tilde{\Phi}_{\alpha\alpha'}(lk;l'k')X_{\beta'}(l'k';lk), \tag{4.15}$$

where

$$X_{\beta'}(l'k';lk)\equiv X_{\beta'}(l'k')-X_{\beta'}(lk). \tag{4.16}$$

We note that when the distortion parameters vanish (4. 15) reduces to (2. 3). It is clear from (3. 8a) that $\Phi_\alpha(l\,k)$ is independent of l, although for convenience we shall retain the formal l dependence in our notation.

Since $\Phi_\alpha(l\,k)$ has no terms of zero order in $\eta_{\alpha\beta}$ and $\bar{d}_\alpha(k)$, we can to lowest order replace $\omega(\vec{0},j)$ and $\hat{e}_\alpha(\vec{0},kj)$ in (4. 14) by $\tilde{\omega}(\vec{0},j)$ and $\tilde{e}_\alpha(\vec{0},kj)$, the undistorted-lattice quantities, obtaining the result

$$\sum_{k'\alpha'}\Gamma_{\alpha\alpha'}(kk')\Big[\sum_{l''k''\alpha''}\bar{d}_{\alpha''}(k'')\tilde{\Phi}_{\alpha'\alpha''}(0k';l''k'') + \sum_{\alpha''\beta''}\eta_{\alpha''\beta''}\sum_{l''k''}\tilde{\Phi}_{\alpha'\alpha''}(0k';l''k'') \times X_{\beta''}(l''k'';0k')\Big]=0, \tag{4. 17}$$

where

$$\Gamma_{\alpha\alpha'}(kk') \equiv (m_k m_{k'})^{-1/2}\sum_j{}' \frac{\tilde{e}_\alpha(\vec{0},kj)\tilde{e}_{\alpha'}(\vec{0},k'j)}{\tilde{\omega}^2(\vec{0},j)}\;. \tag{4. 18}$$

It can be seen that $\Gamma_{\alpha\alpha'}(kk')$ is an effective inverse of the singular matrix $\tilde{\Phi}_{\alpha\alpha'}(0k;l'k')$ in the sense that by use of (3. 18), Eq. (4. 17) can be written as

$$\bar{d}_\alpha(k)+D_\alpha-\sum_{k'\alpha'}\Gamma_{\alpha\alpha'}(kk')\sum_{\alpha''\beta''}\eta_{\alpha''\beta''}S_{\alpha'\alpha''\beta''}(k')=0, \tag{4. 19}$$

where

$$S_{\alpha'\alpha''\beta''}(k')\equiv\sum_{l''k''}\tilde{\Phi}_{\alpha'\alpha''}(0k;l''k'')X_{\beta''}(0k';l''k'') \tag{4. 20}$$

and where D_α denotes the α component of a constant vector independent of k. Such a vector corresponds to a uniform displacement of the crystal, which cannot affect its physical properties. More formally, by use of (3. 8b) it can be confirmed that D_α makes no contribution to any of the expressions we have derived and can therefore be set equal to zero. We thus obtain from (4. 19) the following relation between $\bar{d}_\alpha(k)$ and the external strains:

$$\bar{d}_\alpha(k)=\sum_{\alpha'\beta'}\eta_{\alpha'\beta'}\varphi_{\alpha'\beta'\alpha}(k), \tag{4. 21}$$

where

$$\varphi_{\alpha'\beta'\alpha}(k)\equiv\sum\Gamma_{\alpha\alpha''}(kk'')\,S_{\alpha''\alpha'\beta'}(k''). \tag{4 . 22}$$

In some of the manipulations later on we shall use the symmetry property

$$\Gamma_{\alpha\alpha'}(kk')=\Gamma_{\alpha'\alpha}(k'k). \tag{4.23}$$

Substituting (4. 21) in (4. 15) leads by the use of various properties of the CP's to the result

$$\Phi_\alpha(l\,k)=0, \tag{4. 24}$$

which is thus seen to be necessary as well as sufficient for the satisfaction of (4. 14). It should be stressed, however, that (4. 24) depends upon our approximation of dropping terms of third and higher order $\bar{u}_\alpha(l\,k)$ in H^A. For example, had we retained the term cubic in $\bar{u}_\alpha(l\,k)$ in H^A, a contribution to ΔF linear in $\Phi_\alpha(lk)$ would have appeared in (4. 12), giving rise to a temperature-dependent but η-indepent additional term in (4. 21) which in turn gives rise to a temperature-dependent nonzero value for $\Phi_\alpha(l\,k)$. Clearly, such a term is not associated with thermal expansion, but represents instead a higher-order anharmonic effect in which the thermal motion of the atoms slightly displaces their mean position from rest positions at which the net force vanishes. Although this displacement is required to vanish by symmetry in the large class of parameter-free crystals, for which (4. 24) holds to all orders, in general (4. 24) is only an approximate result. We mention this point to emphasize that our results apply to all crystals in the order of approximation we are using and are not restricted to parameter-free crystals. As a consequence of (4. 24) we obtain from (4. 12) the further approximate results

$$\Delta F=0 \tag{4. 25}$$

and, from (4. 7), (4. 8), and (4. 10),

$$F=\Phi_0+F^{\mathrm{qh}}. \tag{4. 26}$$

We now wish to express the right-hand side of (4. 26) in terms of $\bar{d}_\alpha(k)$ and $\eta_{\alpha\beta'}$ and then substitute (4. 21) and minimize with respect to $\eta_{\alpha\beta}$. In terms of undistorted-lattice CP's and coordinates the static term is found [9] to have the form

$$\Phi_0=\tilde{\Phi}_0+\tfrac{1}{2}\sum_{ll'}\tilde{\Phi}_{\alpha\alpha'}(l\,k;l'k')\,\bar{d}_\alpha(k)\,\bar{d}_{\alpha'}(k') +\sum_l\bar{d}_\alpha(k)\eta_{\alpha'\beta'}\sum_{l'}\tilde{\Phi}_{\alpha\alpha'}(l\,k;l'k')\,X_{\beta'}(l'k') +\tfrac{1}{2}\sum\eta_{\alpha\beta}\eta_{\alpha'\beta'}\sum_{ll'}\tilde{\Phi}_{\alpha\alpha'}(l\,k;l'k')\,X_\beta(l\,k)X_{\beta'}(l'k'). \tag{4. 27}$$

Since the last two terms in (4. 27) contain terms linear and quadratic in $X_\beta(l\,k)$, it might be supposed that the surface of the crystal, where these coordinates are large, makes a substantial contribution to the summations. Such a surface dependence would be undesirable for many reasons, including the possibility that large coefficients would spoil the approximation of keeping only terms of lowest order in the strain parameters, and also because the useful condition (3. 13a), which holds in the volume of the crystal, breaks down near the surface. It is possible, however, to write (4. 27) in a surface-independent form by use of (3. 8b), which depends only on invariance of the potential energy and its derivatives to over-all translation of the crystal and does not involve periodicity. Thus in the third term of (4.27) we can make the replacement

$$X_{\beta'}(l'k') \to X_{\beta'}(l'k';lk). \tag{4.28}$$

The last term of (4.28) can also be shown to depend only on the difference between position vectors by following a procedure given by Leibfried and Ludwig[5] and applied by Maradudin[2] to the primitive lattice case. The generalization to nonprimitive lattices involves a coefficient $\hat{C}_{\alpha\beta\alpha'\beta'}$ defined as follows:

$$\hat{C}_{\alpha\beta\alpha'\beta'} = -\frac{1}{2\tilde{v}} \sum_{lkk'} \Phi_{\alpha\beta}(0k;l'k')X_{\beta'}(lk';0k)X_{\alpha'}(lk';0k), \tag{4.29}$$

where $\tilde{v}$ denotes the volume of a unit cell in the undistorted lattice. Since terms in (4.29) with large position-vector differences have small CP's, $\hat{C}_{\alpha\beta\alpha'\beta'}$ is not sensitive to surface terms.

It can be shown[9] that the expression (4.27) for Φ_0 can be rewritten in the form

$$\Phi_0 = \tilde{\Phi}_0 + \tfrac{1}{2}\sum_{ll'} \tilde{\Phi}_{\alpha\alpha'}(lk;l'k')\,\bar{d}_\alpha(k)\,\bar{d}_{\alpha'}(k') + \sum \bar{d}_\alpha(k)\eta_{\alpha'\beta'}\sum \tilde{\Phi}_{\alpha\alpha'}(lk;l'k')X_{\beta'}(l'l;k'k) + \tfrac{1}{2}N\tilde{v}\sum \eta_{\alpha\beta}\eta_{\alpha'\beta'}\tilde{C}_{\alpha\beta\alpha'\beta'}, \tag{4.30}$$

where

$$\tilde{C}_{\alpha\beta\alpha'\beta'} = \hat{C}_{\alpha\alpha'\beta\beta'} + \hat{C}_{\alpha\beta'\alpha'\beta} - \hat{C}_{\alpha\beta\alpha'\beta'}. \tag{4.31}$$

In this formulation the sensitivity to surface terms has been eliminated.

Returning to the quasiharmonic part of the free energy, we note that to lowest order in the distortion parameters we can write

$$F^{\text{qh}} = \tilde{F}^h + \sum_{\alpha\beta} F_{\alpha\beta}\,\eta_{\alpha\beta} + \sum_{\alpha k} F_\alpha(k)\,\bar{d}_\alpha(k), \tag{4.32}$$

where from (4.11)

$$\tilde{F}^h = \beta^{-1}\sum_{\vec{q},j} \ln\left\{2\sinh\left[\frac{\beta\hbar\tilde{\omega}(\vec{q},j)}{2}\right]\right\}, \tag{4.33}$$

$$F_{\alpha\beta} = \left\{\frac{\partial F^{\text{qh}}}{\partial\eta_{\alpha\beta}}\right\}_0 = \frac{\hbar}{2}\sum_{\vec{q},j}\coth\left[\frac{\beta\hbar\tilde{\omega}(\vec{q},j)}{2}\right]\left[\frac{\partial\omega(\vec{q},j)}{\partial\eta_{\alpha\beta}}\right]_0, \tag{4.34}$$

$$F_\alpha(k) = \left\{\frac{\partial F^{\text{qh}}}{\partial\bar{d}_\alpha(k)}\right\}_0 = \frac{\hbar}{2}\sum_{\vec{q},j}\coth\left[\frac{\beta\hbar\tilde{\omega}(\vec{q},j)}{2}\right]\left[\frac{\partial\omega(\vec{q},j)}{\partial\bar{d}_\alpha(k)}\right]_0. \tag{4.35}$$

In (4.34) and (4.35) the partial derivatives are defined to be taken with all other parameters describing the distortion held constant and evaluated with all the distortion parameters set equal to zero.

By using (3.19) to evaluate the partial derivatives, we obtain the expressions

$$F_{\alpha\beta} = \sum_{\vec{q},j} f(\vec{q},j,\beta)\,d^{(1)}_{\alpha\beta}(\vec{q},j), \tag{4.36}$$

$$F_\alpha(k) = \sum_{\vec{q},j} f(\vec{q},j,\beta)\,d^{(2)}_\alpha(\vec{q},kj), \tag{4.37}$$

where $d^{(1)}_{\alpha\beta}(\vec{q},j)$ and $d^{(2)}_\alpha(\vec{q},kj)$ are given, respectively, by (3.20) and (3.22) and where

$$f(\vec{q},j,\beta) \equiv \hbar[4\tilde{\omega}(\vec{q},j)]^{-1}\coth[\tfrac{1}{2}\beta\hbar\tilde{\omega}(\vec{q},j)]. \tag{4.38}$$

The contribution to the sums in (4.36) and (4.37) from $\vec{q}$ and j corresponding to acoustic modes $[\tilde{\omega}(\vec{0},j)=0]$ is nondivergent, since when (3.20) and (3.22) are substituted, the summation over k' and k'' vanishes by virtue of (3.8b) and the fact that the eigenvectors weighted by $m_k^{-1/2}$ corresponding to these modes are independent of k.

We now wish to eliminate $\bar{d}_\alpha(k)$ from our expressions for Φ_0 and F^{qh} by substitution of (4.21). After some algebra we obtain

$$\Phi_0 = \tilde{\Phi}_0 + \tfrac{1}{2}N\tilde{v}\sum \eta_{\alpha\beta}\eta_{\alpha'\beta'}C_{\alpha\beta\alpha'\beta'}, \tag{4.39}$$

where

$$C_{\alpha\beta\alpha'\beta'} \equiv \tilde{C}_{\alpha\beta\alpha'\beta'} - \frac{1}{\tilde{v}}\sum_{\alpha''k'} \varphi_{\alpha\beta\alpha''}(k)\,S_{\alpha''\alpha'\beta'}(k'). \tag{4.40}$$

It can easily be shown that (4.40) is identical to the expression for the elastic constants of nonionic crystals in the harmonic approximation derived by Born and Huang using the method of long waves.[4]

Finally, we write from (4.21), (4.32), and (4.39) the result

$$F = \tilde{\Phi}_0 + \tfrac{1}{2}N\tilde{v}\sum \eta_{\alpha\beta}\eta_{\alpha'\beta'}C_{\alpha\beta\alpha'\beta'} + \tilde{F}^h + \sum_{\alpha\beta} F_{\alpha\beta}\eta_{\alpha\beta} + \sum F_{\alpha'}(k')\sum_{\alpha\beta}\eta_{\alpha\beta}\varphi_{\alpha\beta\alpha'}(k). \tag{4.41}$$

By imposing the equilibrium condition

$$dF/d\eta_{\alpha\beta} = 0, \tag{4.42}$$

we obtain the result

$$N\tilde{v}\sum_{\alpha'\beta'}\eta_{\alpha'\beta'}C_{\alpha\beta\alpha'\beta'} + F_{\alpha\beta} + \sum F_{\alpha'}(k')\varphi_{\alpha\beta\alpha'}(k') = 0. \tag{4.43}$$

A formal solution to (4.43) is

$$\eta_{\alpha\beta} = -(N\tilde{v})^{-1}\sum_{\alpha'\beta'} C^{-1}_{\alpha\beta\alpha'\beta'} \times \left[F_{\alpha'\beta'} + \sum F_{\alpha''}(k')\varphi_{\alpha'\beta'\alpha''}(k')\right], \tag{4.44}$$

where $C^{-1}_{\alpha\beta\alpha'\beta'}$ is the tensor inverse to $C_{\alpha\beta\alpha'\beta'}$ in the sense

$$\sum_{\alpha''\beta''} C^{-1}_{\alpha\beta\alpha''\beta''} C_{\alpha''\beta''\alpha'\beta'} = \delta_{\alpha\alpha'}\,\delta_{\beta\beta'}\,. \tag{4.45}$$

The $C^{-1}_{\alpha\beta\alpha'\beta'}$'s are the elastic compliances, written as components of a fourth-rank tensor. Substitution of (4.44) into (4.21) gives $\bar{d}_\alpha(k)$ for a thermally expanding lattice. The phonon frequencies as a function of temperature are obtained by substituting these results in (3.19), completing the formal solution of the problem. We note that $\bar{d}_\alpha(k)$, $\eta_{\alpha\beta}$, and consequently the shift in phonon frequencies vanish as expected when the anharmonic CP's are zero. For the case of a primitive lattice our results reduce to the equations given by Maradudin,[2] who applied his expressions to central-force models for cubic Bravais crystals. An application of our more general results to a nonprimitive lattice is presented in Sec. V.

V. APPLICATION TO CENTRAL-FORCE MODEL FOR ZIRCONIUM HYDRIDE

The application of the preceding formal results to zirconium hydride provides an illustration of some practical interest, since phonon frequency distributions for this substance are required over a wide range of temperatures for use in describing its properties as a reactor moderator. It is possible to carry out a rather detailed calculation by using a computer code based on a harmonic central-force model for zirconium hydride[6,12] to provide the eigenvectors and normal-mode frequencies for the undistorted lattice. In this model, ZrH_2 is assumed to have the parameter-free CaF_2 (fluorite) structure, consisting of a face-centered cubic lattice of zirconium atoms interpenetrated by a simple cubic lattice of hydrogen atoms spaced at a distance equal to one-half the dimension of the zirconium cube.[13] Thus the Zr atoms occupy sites of O_h symmetry, while the H atoms occupy sites of T_d symmetry. This symmetry leads to considerable simplification in the calculation of the elastic constants and the distortion parameters. For example, the following relation holds for the quantity defined by (4.20):

$$S_{\alpha\alpha'\beta'}(k) = 0 \tag{5.1}$$

for all k if any two subscripts are equal. As a consequence of (5.1) we obtain from (4.22) the result

$$\varphi_{\alpha'\beta'\alpha}(k) = 0, \text{ if } \alpha' = \beta'\,. \tag{5.2}$$

Together with (4.40), Eqs. (5.1) and (5.2) imply

$$C_{\alpha\beta\alpha'\beta'} = \tilde{C}_{\alpha\beta\alpha'\beta'}, \text{ if } \alpha = \beta \text{ and/or } \alpha' = \beta'\,. \tag{5.3}$$

Further consequences of the lattice symmetry are the vanishing of $F_\alpha(k)$ [(4.35)],

$$F_\alpha(k) = 0, \tag{5.4}$$

and the isotropy of $F_{\alpha\beta}$ [(4.34)],

$$F_{\alpha\beta} = \delta_{\alpha\beta} F, \tag{5.5}$$

where F is defined by this equation. From (4.36) and (5.5) we can write

$$F = \sum_{\vec{q},j} f(\vec{q},j,\beta)\, F(\vec{q},j)\,, \tag{5.6}$$

where

$$F(\vec{q},j) = \tfrac{1}{3} \sum_{kk'\alpha\alpha'\alpha''} \tilde{e}^{*}_{\alpha}(\vec{q},kj)\, \tilde{e}_{\alpha'}$$
$$\times (\vec{q},k'j)\, d_{\alpha\alpha';\alpha''\alpha''}(\vec{q},kk'). \tag{5.7}$$

The results (5.1), (5.4), and (5.5) can be proved in a straightforward fashion by using the transformation properties of the CP's, eigenvectors, and lattice coordinates as given, for example, by Maradudin and Vosko.[14] We omit the detailed proof here.

Central-force-model expressions for the first- and second-order CP's are given by Born and Huang.[15] For the third-order CP's we obtain

$$\tilde{\Phi}_{\alpha\alpha'\alpha''}(0k;l'k';l''k'') = 4(\delta_{0l'}\,\delta_{kk'} - \delta_{0l''}\,\delta_{k'k''})$$
$$\times \{-2X_\alpha X_{\alpha'} X_{\alpha''} \Psi^{(3)}_{k'k''} - (\delta_{\alpha\alpha'} X_{\alpha''} + \delta_{\alpha\alpha''} X_{\alpha'}$$
$$+ \delta_{\alpha'\alpha''} X_\alpha)\, \Psi^{(2)}_{k'k''}\}_{\vec{x}(l'k'l''k'')} \tag{5.8a}$$

(the case $l' = l'' = 0$, $k = k' = k''$ excluded) and

$$\tilde{\Phi}_{\alpha\alpha'\alpha''}(000,kkk) = 4 \sum_{l'k'} \{2X_\alpha X_{\alpha'} X_{\alpha''} \Psi^{(3)}_{kk'}$$
$$+ (\delta_{\alpha\alpha'} X_{\alpha''} + \delta_{\alpha\alpha''} X_{\alpha'} + \delta_{\alpha'\alpha''} X_\alpha)\, \Psi^{(2)}_{kk'}\}_{\vec{x}(0k;l'k')}\,. \tag{5.8b}$$

In these equations δ_{0l} stands for the product $\delta_{0l_x}\,\delta_{0l_y}\,\delta_{0l_z}$, where l_x, l_y, and l_z are the cell indices of the lth unit cell.

In (5.8) the potential energy $\Psi_{kk'}$ between two particles of types k and k' is regarded as a function of the square of the distance and $\Psi^{(n)}_{kk'}$ denotes the nth derivative taken with respect to the squared distance. The subscripts on the curly brackets indicate the arguments of the enclosed functions. The formal provision is made that $\Psi_{kk'}$ and its derivatives vanish for zero value of the argement.

The condition that the lattice be in a configuration corresponding to vanishing stress imposes the requirement[15]

$$\sum_{lkk'} \{X_\alpha X_\beta \Psi^{(1)}_{kk'}\}_{\vec{x}(0k;lk')} \equiv 0. \tag{5.9}$$

Then the $\tilde{C}_{\alpha\beta\alpha'\beta'}$ contribution to the elastic constants in the harmonic approximation can be written as follows:

$$\bar{C}_{\alpha\beta\alpha'\beta'} = \frac{\hat{2}}{\tilde{v}} \sum_{lkk'} \{X_\alpha X_\beta X_{\alpha'} X_{\beta'} \Psi^{(2)}_{kk'}\}_{\vec{X}(0k;\, lk')} \cdot \qquad (5.10)$$

To obtain the central-force-model expression for $F(\vec{q},j)$ we substitute (5.8) in (3.19) and use (5.7) to obtain after some manipulation the result

$$F(\vec{q},j) = \tfrac{4}{3} \sum_{lkk'k''} \{2r^2 \Psi^{(3)}_{k'k''} [\vec{e}(\vec{q},k'j)\cdot\vec{X}][\vec{e}(\vec{q},kj)^*\cdot\vec{X}] + r^2 \Psi^{(2)}_{k'k''} [\vec{e}(\vec{q},k'j)\cdot\vec{e}(\vec{q},kj)^*]$$

$$+ 2\mathrm{Re}\,\Psi^{(2)}_{k'k''} [\vec{e}(\vec{q},k'j)\cdot\vec{X}][\vec{e}(\vec{q},kj)^*\cdot\vec{X}]\}_{\vec{X}(0k'';\, lk')} \cdot [\delta_{kk'} - \delta_{k''k}\, e^{2\pi i \vec{q}\cdot\vec{x}(l)}], \qquad (5.11)$$

where in terms of the eigenvectors defined by (3.23)

$$e_\alpha(\vec{q},kj) \equiv (m_k)^{-1/2} \tilde{e}_\alpha(\vec{q},kj) \qquad (5.12)$$

and $r^2 = \vec{X}\cdot\vec{X}$. The dependence of $F(\vec{q},j)$ on $\vec{q}$ is such that the summation over $\vec{q}$ in (5.6) can be restricted to the irreducible element of the first Brillouin zone, with appropriate weighting for boundary points.[12]

From (4.44), using (5.4) and (5.5), we now obtain for the distortion parameters the expression

$$\eta_{\alpha\beta} = -(F/\tilde{V}) \sum_{\alpha'} C^{-1}_{\alpha\beta\alpha'\alpha'}$$

$$= -(F/\tilde{V})[C^{-1}_{\alpha\alpha 11} + C^{-1}_{\alpha\alpha 22} + C^{-1}_{\alpha\alpha 33}]\,\delta_{\alpha\beta}$$

$$= -\delta_{\alpha\beta}(F/\tilde{V})[C^{-1}_{1111} + 2C^{-1}_{1122}] = \delta_{\alpha\beta}\,\eta(T), \qquad (5.13)$$

where $\tilde{V}$ denotes the volume of the undistorted crystal and where the final equation defines $\eta(T)$. We have used the fact that the elastic compliances have the same symmetry properties as the elastic constants. On switching to the Voigt notation[4] and noting the relations[16]

$$C^{-1}_{11} = \frac{C_{11} + C_{12}}{(C_{11} + 2C_{12})(C_{11} - C_{12})}, \qquad (5.14a)$$

$$C^{-1}_{12} = \frac{-C_{12}}{(C_{11} + 2C_{12})(C_{11} - C_{12})}, \qquad (5.14b)$$

we can write

$$\eta(T) = -(1/3\tilde{V})F/B, \qquad (5.15)$$

where B is the bulk modulus, given in the harmonic approximation by

$$B = \tfrac{1}{3}(C_{11} + 2C_{12}) = \tfrac{1}{3}(\tilde{C}_{11} + 2\tilde{C}_{12}). \qquad (5.16)$$

We have used (5.3) to write B in terms of the $\tilde{C}_{\alpha\beta\alpha'\beta'}$'s. The diagonality of $\eta_{\alpha\beta}$ gives immediately by (4.21) and (5.2) the result that $\bar{d}_\alpha(k)$ vanishes.

We can use (5.13) and the fact that volume-expansion ratio is given by $[\det(1 + 2\eta_{\alpha\beta})]^{1/2}$ to obtain an expression for the coefficient of linear expansion λ:

$$\lambda \equiv \frac{1}{3V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{3(1+2\eta)^{3/2}} \frac{d}{dT}(1+2\eta)^{3/2}$$

$$= \frac{1}{1+2\eta}\,\frac{d\eta}{dT} = -F'[3\tilde{V}B(1+2\eta)]^{-1}, \qquad (5.17)$$

where V is the volume of the distorted crystal and

$$F' = \sum_{\vec{q},j} \frac{df(\vec{q},j,\beta)}{dT} F(\vec{q},j)$$

$$= \frac{\hbar^2}{8k_B T^2} \sum_{\vec{q},j} \sinh^{-2}[\tfrac{1}{2}\beta\hbar\,\tilde{\omega}(\vec{q},j)]\,F(\vec{q},j), \qquad (5.18)$$

as follows from differentiating (4.38).

Finally, noting (5.3), (5.7), and (5.13), we can obtain from (3.19) an expression for the square of the distorted-lattice phonon frequencies in the following simple form:

$$\omega^2(\vec{q},j) = \tilde{\omega}^2(\vec{q},j) + 3\eta(T)F(\vec{q},j). \qquad (5.19)$$

As mentioned above, the undistorted-lattice eigenvalues and eigenvectors $\tilde{\omega}(\vec{q},j)$ and $\tilde{e}(\vec{q},kj)$ are obtainable from a previously developed harmonic central-force model.[6] Four "force constants" appear in this model, denoted by μ, γ, ν, and δ and defined as follows (where a denotes the fcc lattice constant):

$$\mu = a^2 \Psi^{(2)}_{\mathrm{ZH}}(r^2), \quad r = \tfrac{1}{4}\sqrt{3}\,a \qquad (5.20a)$$

$$\gamma = a^2 \Psi^{(2)}_{\mathrm{ZZ}}(r^2), \quad r = \tfrac{1}{2}\sqrt{2}\,a \qquad (5.20b)$$

$$\nu = a^2 \Psi^{(2)}_{\mathrm{HH}}(r^2), \quad r = \tfrac{1}{2}a \qquad (5.20c)$$

$$\delta = a^2 \Psi^{(2)}_{\mathrm{HH}}(r^2), \quad r = \tfrac{1}{2}\sqrt{2}\,a. \qquad (5.20d)$$

In (5.20a), for example, $\Psi^{(2)}_{\mathrm{ZH}}(r^2)$ denotes the value of the second derivative with respect to the square of the distance of the central-force potential between a zirconium atom and a nearest-neighbor hydrogen atom at a distance $\frac{1}{4}\sqrt{3}a$. Each Zr atom has eight nearest-neighbor H atoms at a distance $\frac{1}{4}\sqrt{3}a$ and twelve next-nearest-neighbor Zr atoms at a distance $\frac{1}{2}\sqrt{2}a$, for which γ is the appropriate force constant. Each H atom has six next-nearest-neighbor H atoms at a distance $\frac{1}{2}\sqrt{2}a$, for which ν and δ

are, respectively, the appropriate force constants. If we label the Zr atom and the two H atoms in a unit cell by $k = 1, 2, 3$, respectively, we can write in the notation of (5.8)

$$\begin{aligned} &\Psi^{(2)}_{12}(r^2) = \Psi^{(2)}_{21}(r^2) = \mu/a^2, && r = \tfrac{1}{4}\sqrt{3}a \\ &\Psi^{(2)}_{11}(r^2) = \gamma/a^2, && r = \tfrac{1}{2}\sqrt{2}a \qquad (5.21) \\ &\Psi^{(2)}_{23}(r^2) = \Psi^{(2)}_{33}(r^2) = \delta/a^2, && r = \tfrac{1}{2}\sqrt{2}a. \end{aligned}$$

At distances greater than $\frac{1}{2}\sqrt{2}a$ all interatomic forces are assumed negligible.

The following force constants were found[6] to give a phonon frequency distribution in agreement with neutron scattering and specific-heat data:

$$\begin{aligned} \mu &= 0.49\times 10^5\ g/\mathrm{sec}^2, \\ \gamma &= 0.14\times 10^5\ g/\mathrm{sec}^2, \\ \nu &= 0.6\times 10^4\ g/\mathrm{sec}^2, \\ \delta &= 0.15\times 10^4\ g/\mathrm{sec}^2. \end{aligned} \qquad (5.22)$$

The first derivatives $\Psi^{(1)}_{kk}$ were chosen to vanish:

$$\Psi^{(1)}_{kk'}(r^2) \equiv 0 \qquad (5.23)$$

when r has the values indicated in (5.21), thus guaranteeing the satisfaction of (5.9). [Equation (2.3) is satisfied identically by virtue of the lattice symmetry regardless of the choice for $\Psi^{(1)}_{kk'}$.] Then by using (5.10) and noting that $\bar{v} = \frac{1}{4}a^3$ for a fcc lattice we obtain from (5.16) and previous equations the result

$$B = (4/3a)(2\gamma + 4\delta + \tfrac{3}{8}\mu + \tfrac{1}{2}\nu). \qquad (5.24)$$

Choosing $a = 4.79$ Å[13] and using the values (5.22), we obtain

$$\begin{aligned} B &= 0.1541\times 10^{13}\ \mathrm{dyn/cm^2} \\ &= 2.235\times 10^{7}\ \mathrm{lb/in.^2}, \end{aligned}$$

which is the expected order of magnitude.[13]

Next we can select a set of values for the third-derivative force constants $\Psi^{(3)}_{kk'}$ and test our choice by comparing with experiment the linear-expansion coefficient calculated from (5.17). A special choice for these force constants greatly simplifies the calculation of $F(\vec{q}, j)$. We first observe, using (3.18) and orthonormality of the eigenvectors, that the harmonic-model normal-mode frequencies can be written as

$$\begin{aligned} \tilde{\omega}^2(\vec{q}, j) &= \sum \tilde{e}_\alpha(\vec{q}, k, j)^* \tilde{d}_{\alpha\alpha'}(\vec{q}, kk')\tilde{e}_{\alpha'}(\vec{q}, k') \\ &= 4 \sum_{lkk'k''} \{\Psi^{(2)}_{kk''}[\vec{e}(\vec{q}, k'j)\cdot\vec{X}][\vec{e}(\vec{q}, kj)^*\cdot\vec{X}]\}_{\vec{X}(0k;lk'')} \cdot [\delta_{kk'} - \delta_{k''k}e^{2\pi i\vec{q}\cdot\vec{X}(l)}], \end{aligned} \qquad (5.25)$$

where the second expression is obtained by using central-force-model expressions for the CP in (3.12). Substituting (5.25) in (5.11) and using the fact that $\tilde{\omega}^2(\vec{q}, j)$ is real, we can write

$$\begin{aligned} F(\vec{q}, j) = \tfrac{4}{3} \sum_{lkk'k''} &\{2r^2\Psi^{(3)}_{k''k}[\vec{e}(\vec{q}, k''j)\cdot\vec{X}][\vec{e}(\vec{q}, k'j)^*\cdot\vec{X}] + r^2\Psi^{(2)}_{k''k}[\vec{e}(\vec{q}, k''j)\cdot\vec{e}(\vec{q}, kj)^*]\}_{\vec{X}(0k;lk'')} \\ &\cdot [\delta_{k'k''} - \delta_{kk'}e^{2\pi i\vec{q}\cdot\vec{X}(l)}] + \tfrac{2}{3}\tilde{\omega}^2(\vec{q}, j). \end{aligned} \qquad (5.26)$$

If we choose the third-derivative force constants so that

$$\{r^2\Psi^{(3)}_{k'k}\}_{\vec{X}(0k;lk)} = A\{\Psi^{(2)}_{k'k}\}_{\vec{X}(0k;lk')}, \qquad (5.27)$$

where A is a dimensionless proportionality constant, we than arrive at the result

$$\begin{aligned} F(\vec{q}, j) &= \tfrac{4}{3} \sum_{lkk'k''} \{r^2\Psi^{(2)}_{k''k}\}_{\vec{X}(0k;lk'')}[\vec{e}(\vec{q}, k''j)\cdot\vec{e}(\vec{q}, k'j)^*]\cdot[\delta_{k'k''} - \delta_{kk'}e^{2\pi i\vec{q}\cdot\vec{X}(l)}] + \tfrac{2}{3}(A+1)\,\tilde{\omega}^2(\vec{q}, j) \\ &= \tfrac{4}{3} \sum_{lkk'} \{r^2\Psi^{(2)}_{kk'}\}_{\vec{X}(0k;lk'')}[\,|\vec{e}(\vec{q}, k'j)|^2 - \vec{e}(\vec{q}, kj)\cdot\vec{e}(\vec{q}, kj)^* e^{2\pi i\vec{q}\cdot\vec{X}(l)} + \tfrac{2}{3}(A+1)\,\tilde{\omega}^2(\vec{q}, j) \end{aligned} \qquad (5.28)$$

by use of (5.25). The summation over l, k, and k' can be carried out explicitly and a somewhat lengthy expression obtained for $F(\vec{q}, j)$ in terms of the force constants (5.21), but (5.28) is already in a convenient form for evaluation by computer.

We can now select a trial value for A and perform a calculation of the coefficient of linear expansion. A crude means of making a first guess for A is to assume a simple Lennard-Jones form for the central force interatomic potential; for example, we assume for the potential the form

$$\Psi(y) = cy^{-6} - by^{-3}, \tag{5.29}$$

where $y = r^2$, at values of r in the neighborhood of an equilibrium separation distance $\tilde{r}$ in the undistorted lattice. Then the condition

$$\Psi^{(1)}(\tilde{y}) = 0,$$

where $\tilde{y} = \tilde{r}^2$, enables us to eliminate c from (5.29), thereby obtaining

$$\Psi(y) = b(\tfrac{1}{2}\tilde{y}^3 y^{-6} - y^{-3}). \tag{5.30}$$

Using (5.30), we find that

$$\tilde{r}^2 \Psi^{(3)}(\tilde{r}^2) = -12\Psi^{(2)}(\tilde{r}^2),$$

which according to (5.27) suggests the choice

$$A = -12.0\ .$$

A calculation of λ for $A = -12.0$ using 520 values for $\vec{q}$ in the irreducible element leads to the values

$$\lambda = 1.125\times10^{-5}/{}^\circ\mathrm{K} \quad \text{at } T = 300\,{}^\circ\mathrm{K}$$

$$\lambda = 2.28\times10^{-5}/{}^\circ\mathrm{K} \quad \text{at } T = 800\,{}^\circ\mathrm{K}.$$

The most nearly comparable experimental measurements appear to have been made by Kempter, Elliott, and Geschneider[17] for $\mathrm{ZrH}_{1.96}$ in the slightly tetragonal ϵ phase. For randomly oriented polycrystalline material between 24 and 300 °C they observed an average linear expansion coefficient of $0.93\times10^{-5}/{}^\circ\mathrm{K}$, which with our calculated value is in qualitative agreement. By varying the value of A within reasonable limits we could obtain an exact fit to an observed value for α at a given temperature if such data were available. (As an example of dependence of λ on A, we note that a calculation with $A = -10.0$ gave a value of $0.86\times10^{-5}/{}^\circ\mathrm{K}$ for λ at $T = 300\,{}^\circ\mathrm{K}$.) For $A = -12.0$ the calculated value for the distortion parameter η is 0.019 56 at $T = 300\,{}^\circ\mathrm{K}$ and 0.029 12 at 800 °K. The shifted phonon frequencies can then be obtained from (5.19). Table I gives a few examples of calculated values for $\tilde{\omega}(\vec{q},j)$ and $\omega(\vec{q},j)$ at 300 °K (see Fig. 1).

Figure 1 shows phonon frequency distributions for ZrH_2 based on 520 $\vec{q}$-point (4680 frequencies) calculations at 300 and 800 °K. A shift to lower frequencies is apparent at the higher temperature, the central frequency of the optical part being decreased by about 15%. (The distribution at 300 °K calculated here is not in agreement with neutron data, since we have not reevaluated the harmonic force constants to fit the data in the presence of anharmonicity. The frequency shifts introduced by the anharmonicity displace the optical peak shown here from its observed position centered around 0.14 eV. We have not adjusted the force constants to restore agreement, since our purpose here is to illustrate the effects of thermal expansion rather than provide accurate phenomenological fits.) The amplitude-weighted distributions used in neutron scattering calculations[6] have not been calculated but are expected to be shifted by about the same amount. Of course, these shifts do not give a complete specification of the lowest-order effects of anharmonicity on neutron scattering, since we have not included purely anharmonic phonon frequency shifts of the type calculated by Maradudin and Fein[1] and Cowley[3]. The purely anharmonic shifts reported in those references are somewhat smaller than the thermal-expansion shifts but of the same order of magnitude. The third- and fourth-order shifts are of opposite sign, the third-order shift

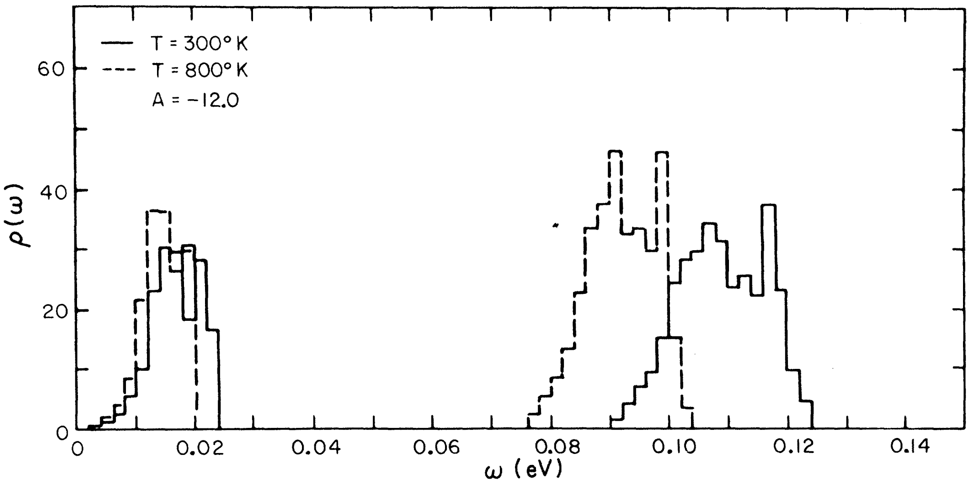

FIG. 1. Phonon frequency distributions for ZrH_2 at 300 °K and 800 °K.

TABLE I. ZrH_2 shifted and unshifted phonon frequencies and values of $F(\vec{q}, j)$ calculated at $T = 300$ °K for $A = -12.0$.

$\vec{q} = (0, 0, 0)a^{-1}$									
$\tilde{\omega}(\vec{q}, j)$ (eV)	0.1375	0.1375	0.1375	0.1139	0.1139	0.1139	0.0	0.0	0.0
$F(\vec{q}, j)$ (eV)^2	−0.1198	−0.1198	−0.1198	−0.08215	−0.08215	−0.08215	0.0	0.0	0.0
$\omega(\vec{q}, j)$ (eV)	0.1090	0.1090	0.1090	0.09029	0.09029	0.09029	0.0	0.0	0.0
$\vec{q} = (\frac{1}{3}, \frac{1}{3}, \frac{1}{3})a^{-1}$									
$\tilde{\omega}(\vec{q}, j)$ (eV)	0.1486	0.1375	0.1363	0.1363	0.1248	0.1248	0.02612	0.01325	0.01325
$F(\vec{q}, j)$ (eV)^2	−0.1423	−0.1221	−0.1165	−0.1165	−0.09762	−0.09762	−0.00445	−0.00083	−0.00083
$\omega(\vec{q}, j)$ (eV)	0.1172	0.1084	0.1083	0.1083	0.09928	0.09928	0.02052	0.01129	0.01129
$\vec{q} = (1, 0, 0)a^{-1}$									
$\tilde{\omega}(\vec{q}, j)$ (eV)	0.1585	0.1489	0.1489	0.1375	0.1257	0.1257	0.03025	0.02081	0.02081
$F(\vec{q}, j)$ (eV)	−0.1653	−0.1418	−0.1418	−0.1177	−0.09696	−0.09696	−0.00601	−0.00232	−0.04232
$\omega(\vec{q}, j)$ (eV)	0.1242	0.1177	0.1177	0.1096	0.1006	0.1006	0.02372	0.01723	0.01723

having the same sign as the thermal-expansion shift, so that there is a partial cancellation of the purely anharmonic shifts. Thus a thermal-expansion calculation like that which we have performed for ZrH_2 probably gives a good estimate of the over-all magnitude of the temperature dependence of the phonon frequencies as they appear in neutron scattering calculations.

ACKNOWLEDGMENT

The author wishes to thank Professor A. A. Maradudin for suggesting this investigation and for clarifying many important points in the course of several discussions.

---

[1] A. A. Maradudin and A. E. Fein, Phys. Rev. 128, 2589 (1962).

[2] A. A. Maradudin, Phys. Status Solidi 2, 1493 (1962).

[3] R. A. Cowley, Advan. Phys. 12, 421 (1963).

[4] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford U. P., Oxford, England, 1954).

[5] G. Leibfried and W. Ludwig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1963), Vol. 12, p. 275.

[6] E. L. Slaggie, J. Phys. Chem. Solids 29, 923 (1968).

[7] J. R. Beyster and J. A. Young, Ann. Rev. Nucl. Sci. 17, 97 (1968).

[8] E. L. Slaggie, USAEC Report No. GA-9162, 1969 (unpublished).

[9] E. L. Slaggie, USAEC Report No. GA-9417, 1968 (unpublished).

[10] See, for example, Eq. (2.9) in Leibfried and Ludwig (Ref. 5).

[11] A. A. Maradudin (unpublished).

[12] E. L. Slaggie, General Atomic Report No. GA-8132, 1967 (unpublished).

[13] General Atomic Report No. GA-471, 1958 (unpublished).

[14] A. A. Maradudin and S. H. Vosko, Rev. Mod. Phys. 40, 1 (1968).

[15] Born and Huang (Ref. 4), Sec. 29.

[16] R. F. S. Hearmon, *An Introduction to Applied Anisotropic Elasticity* (Oxford U. P., Oxford, England, 1961).

[17] C. P. Kempter, R. O. Elliott, and K. A. Gschneider, Jr., J. Chem. Phys. 33, 837 (1960).