Anharmonic Free Energy of Crystals at High Temperatures*

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The general expressions for the high-temperature contributions to the anharmonic free energy at constant volume are simplified for the case of two-body forces for lattices with one or two atoms per unit cell. The quadratic, cubic, and quartic potential-energy coefficients are derived for any lattice for the case of two-body central forces. Accurate calculations of the free-energy contributions, for face-centered cubic and hexagonal close-packed lattices, are described. The calculations are based on two-body central-force interactions, with various ranges of the forces, represented by a Lennard-Jones form. The nearest-neighbor distance was fixed at the value which minimizes the static lattice potential energy. The results for the two lattice types are quite similar, and show a negative anharmonic contribution to the high-temperature specific heat at constant volume. A very simple method of approximating the complicated free-energy expressions is formulated in general and evaluated for the same cases for which accurate calculations are presented. This approximation is based on the replacement of each dynamical matrix of the harmonic lattice dynamics problem by a constant multiple of the unit matrix. Previously published approximations are also compared to the present results, and it is concluded that the approximation developed here is the best one currently available in terms of accuracy and simplicity.

I. INTRODUCTION

THIS paper is concerned with the anharmonic contributions to the free energy of crystals, at temperatures above the Debye temperature. The work is based on the standard treatment of the lattice dynamics problem,[1,2] in which the potential energy of the system of vibrating ions is expanded in a Taylor series in the displacements of the ions from their equilibrium positions. The Hamiltonian for the system, to fourth order in the displacements, can be written as

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_3 + \mathcal{H}_4, \qquad (1.1)$$

where

$$\mathcal{H}_0 = \tfrac{1}{2} \sum_{n,\rho} M_j (\dot{u}_{n\rho})^2 + \tfrac{1}{2} \sum_{nn',\rho\rho'} A_{n\rho,n'\rho'} u_{n\rho} u_{n'\rho'}, \qquad (1.2)$$

$$\mathcal{H}_3 = (1/3!) \sum_{nn'n'',\rho\rho'\rho''} B_{n\rho,n'\rho',n''\rho''} \\ \times u_{n\rho} u_{n'\rho'} u_{n''\rho''}, \qquad (1.3)$$

$$\mathcal{H}_4 = (1/4!) \sum_{n\cdots n''',\rho\cdots\rho'''} C_{n\rho,n'\rho',n''\rho'',n'''\rho'''} \\ \times u_{n\rho} u_{n'\rho'} u_{n''\rho''} u_{n'''\rho'''}. \qquad (1.4)$$

The notation used here, and below, is as follows. The symbol n labels a unit cell in the crystal, j labels an ion in the unit cell, i labels a Cartesian coordinate, M_j is the mass of an ion of type j, u_{nj} is the displacement of ion (n,j) from its equilibrium position, and $\dot{u}_{nj}$ is the time derivative of u_{nj}. There are N unit cells in the crystal, J ions per unit cell, and the total mass of the ions in one unit cell is M_c. The primitive lattice vectors, which give the location of some reference point in each unit cell, are denoted by $\mathbf{r}_n$, the basis vectors are $\mathbf{r}_j$, and the equilibrium position of ion (n,j) is $\mathbf{r}_{nj} = \mathbf{r}_n + \mathbf{r}_j$. It is convenient to use the contractions ν, standing for

the pair (n,j), and ρ, standing for the pair (j,i). Thus

$$A_{nji,n'j'i'} \equiv A_{n\rho,n'\rho'} \equiv A_{\nu i,\nu'i'}, \quad \text{etc.} \qquad (1.5)$$

The usual harmonic approximation is represented by $\mathcal{H}_0$. The normal coordinates of $\mathcal{H}_0$ are enumerated by the wave vectors $\mathbf{k}$ and the polarization index s, there being N values of $\mathbf{k}$ distributed uniformly over the first Brillouin zone, and $3J$ values of s associated with each $\mathbf{k}$. The circular frequencies of the normal modes, $\omega_{\mathbf{k}s}$, are obtained by diagonalization of the dynamical matrices ($a_\mathbf{k}$ matrices)

$$\sum_{\rho'} a_{\mathbf{k},\rho\rho'} v_{\mathbf{k},\rho's} = M_j (\omega_{\mathbf{k}s})^2 v_{\mathbf{k},\rho s}, \qquad (1.6)$$

where

$$a_{\mathbf{k},\rho\rho'} = \sum_{n'} A_{n\rho,n'\rho'} \exp[-i\mathbf{k}\cdot(\mathbf{r}_{nj}-\mathbf{r}_{n'j'})], \qquad (1.7)$$

and where $v_{\mathbf{k},\rho s}$ are components of the eigenvectors of $a_\mathbf{k}$. The following properties of the $a_\mathbf{k}$ matrices, and their eigenvectors, will be found useful:

$$a_\mathbf{k}^\dagger = a_\mathbf{k}; \qquad (1.8)$$

$$a_\mathbf{k}^* = a_{-\mathbf{k}}, \quad \text{hence} \quad v_\mathbf{k}^* = v_{-\mathbf{k}} \text{ can be taken;} \qquad (1.9)$$

$$\sum_\rho M_j v_{\mathbf{k},\rho s} v_{-\mathbf{k},\rho s'} = M_c \delta_{ss'} \text{ (orthogonality);} \qquad (1.10)$$

$$M_j \sum_s v_{\mathbf{k},\rho s} v_{-\mathbf{k},\rho' s} = M_c \delta_{\rho\rho'} \text{ (completeness);} \qquad (1.11)$$

$$\sum_s v_{\mathbf{k},\rho s} (\omega_{\mathbf{k}s})^{-2} v_{-\mathbf{k},\rho's} = M_c [a_\mathbf{k}^{-1}]_{\rho\rho'} = M_c \lambda_{\mathbf{k},\rho\rho'}. \qquad (1.12)$$

The last equation defines $\lambda_\mathbf{k}$ as the matrix inverse to $a_\mathbf{k}$.

It should be pointed out that there are two representations of the diagonal form of $\mathcal{H}_0$ which are commonly used; these are based on normal mode transformations which carry factors like $\exp(i\mathbf{k}\cdot\mathbf{r}_n)$, or $\exp(i\mathbf{k}\cdot\mathbf{r}_{nj})$, respectively. They are related by a unitary transformation. The second representation has been used here because it gives rise to much greater symmetry in $\mathbf{k}$ space of the $a_\mathbf{k}$ matrices, when there is more than one atom per unit cell. This in turn allows a greater simplification of computational problems such as those undertaken in the present work.

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[1] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, England, 1954).
[2] R. E. Peierls, *Quantum Theory of Solids* (Clarendon Press, Oxford, England, 1955).

The Helmholtz free energy for the system (1.1) can be calculated by treating $\mathcal{3C}_3$ and $\mathcal{3C}_4$ as perturbations. $\mathcal{3C}_3$ does not contribute in first order, and so the second-order contribution of $\mathcal{3C}_3$ and the first-order contribution of $\mathcal{3C}_4$ are both considered. The high-temperature limit of these contributions was derived classically by Born and Brody[3] in 1921, while the quantum-mechanical form, valid for all temperatures, was given by Ludwig[4] in 1958. The present calculations are confined to the high-temperature limit. An alternate derivation of the high-temperature forms, in terms of the matrices λ_k, has been given previously[5]; with certain modifications, the results are

$$F_3 = -[(KT)^2/12N]$$
$$\times \sum_{kk'k''} \sum_{n'\cdots n^{iv},\rho\cdots\rho^v} \delta(k+k'+k'')$$
$$\times B_{n\rho,n'\rho',n''\rho''}B_{n\rho',n''',n'''\rho^{iv},n^{iv}\rho^v} \exp[ik\cdot(r_j-r_{j'''})]$$
$$\times \exp[ik'\cdot(r_{n'j'}-r_{n'''j^{iv}})] \exp[ik''\cdot(r_{n''j''}-r_{n^{iv}j^v})]$$
$$\times [\lambda_{k,\rho\rho'''}\lambda_{k',\rho'\rho^{iv}}\lambda_{k'',\rho''\rho^v}+(\hbar/KT)^4(1/240M_jM_{j'})$$
$$\times \delta_{\rho\rho'''}\delta_{\rho'\rho^{iv}}\lambda_{k'',\rho''\rho^v}+\cdots], \quad (1.13)$$

$$F_4 = [(KT)^2/8N]$$
$$\times \sum_{kk'} \sum_{n'n''n''',\rho\cdots\rho'''} C_{n\rho,n'\rho',n''\rho'',n'''\rho'''}$$
$$\times \exp[ik\cdot(r_{nj}-r_{n'j'})] \exp[ik'\cdot(r_{n''j''}-r_{n'''j'''})]$$
$$\times \{\lambda_{k,\rho\rho'}\lambda_{k',\rho''\rho'''}+(\hbar/KT)^2(1/6M_j)\delta_{\rho\rho'}\lambda_{k',\rho''\rho'''}$$
$$-(\hbar/KT)^4(1/720)[(2/M_jM_{j'})a_{k,\rho\rho'}\lambda_{k',\rho''\rho'''}$$
$$-(5/M_jM_{j''})\delta_{\rho\rho'}\delta_{\rho''\rho'''}]+\cdots\}. \quad (1.14)$$

These expressions for F_3 and F_4 differ from those obtained in Ref. 5 in two respects. (1) Certain terms in F_3 involving $k''=0$ have been omitted, since their contribution is of order N^{-1} compared to the other terms. In fact, all remaining terms involving any zero wave vector can be dropped for the same reason, so that those cases for which λ_k does not exist need not be considered. (2) The above expressions retain terms to order T^{-2} in the general high-temperature expansion of F_3 and F_4. These terms have been given by other workers in slightly different form.[4,6]

Several approximate calculations of F_3 and F_4 have been carried out,[4-7] but to date no accurate calculations have been made for any force model for a three-dimensional crystal. The present paper reports the results of accurate calculations for face-centered cubic (fcc) and hexagonal close-packed (hcp) lattices, for the case of two-body central forces represented by a Lennard-Jones form. All of the lengthy numerical work was carried out with the aid of a CDC-1604 digital computer. Even with a high-speed computer, the evaluation of (1.13) and (1.14) is quite impossible without first simplifying the formulas a great deal. Indeed, the straightforward calculation of the T^2 term

in (1.13), for nearest neighbors only for the fcc lattice for any one of the potential models listed in Sec. III below, would require at least 10^{10} years on our computer. By algebraic simplification, this particular calculation was reduced to 14 min of computer time.

One great simplification is obtained by separating the multiple sums over wave vectors in (1.13) and (1.14), and writing them as products of single sums. This can be accomplished at once in (1.14), and also in (1.13) when the δ function is replaced according to

$$\delta(k+k'+k'')=N^{-1}\sum_n \exp[i(k+k'+k'')\cdot r_n]. \quad (1.15)$$

This definition of $\delta(k)$ has been used throughout. Further simplifications of the general formulas, for special cases, are described below. The philosophy of the present work has been to obtain accurate results, with known error limits, for a simple model, rather than to apply the calculations to a particular material. In addition, several approximations have been evaluated by comparison with the accurate results.

In the following, the major consideration has been given to the leading terms of (1.13) and (1.14), since the remaining terms are much simpler to handle. These leading terms, which are proportional to T^2, are denoted by F_{3T} and F_{4T}, respectively. The leading anharmonic contribution to the specific heat at constant volume is then given by

$$C_{VT}=-(2/T)(F_{3T}+F_{4T}). \quad (1.16)$$

II. TWO-BODY FORCES

The harmonic Hamiltonian, $\mathcal{3C}_0$, is already restricted to two-body forces, since the A coefficients couple no more than two different ions. Equations (1.13) and (1.14) can be simplified a great deal when only two-body forces are considered. This is mainly because, for this case, all B and C coefficients which couple more than two different ions vanish, while those nonvanishing B and C coefficients have a high degree of symmetry. The sums over lattice points can therefore be considerably reduced.

The symmetry properties of the potential energy coefficients have been discussed previously by other workers.[8] Those relations of interest are summarized here, with particular reference to two-body forces.

$$A_{n\rho,n'\rho'}=A_{n'\rho',n\rho},$$
$$B_{n\rho,n\rho,n'\rho'}=B_{n\rho,n'\rho',n\rho}=B_{n'\rho',n\rho,n\rho}, \quad (2.1)$$
$$C_{n\rho,n\rho,n\rho,n'\rho'}=C_{n\rho,n\rho,n'\rho',n\rho}=\text{etc.};$$
$$\sum_{\nu'} A_{\nu\nu'}=\sum_{\nu'} B_{\nu\nu\nu'}=\sum_{\nu'} C_{\nu\nu\nu\nu'}=0; \quad (2.2)$$
$$A_{\nu\nu'}=A_{\nu'\nu},$$
$$B_{\nu\nu\nu'}=B_{\nu\nu'\nu}=B_{\nu'\nu\nu}=-B_{\nu\nu'\nu'}=-B_{\nu'\nu\nu'}$$
$$=-B_{\nu'\nu'\nu}, \quad \nu\neq\nu', \quad (2.3)$$
$$C_{\nu\nu\nu\nu'}=C_{\nu\nu\nu'\nu}=\text{etc.}=-C_{\nu\nu\nu'\nu'}=-C_{\nu\nu'\nu\nu'}=\text{etc.}$$
$$=C_{\nu\nu'\nu'\nu'}=C_{\nu'\nu\nu'\nu'}=\text{etc.}, \quad \nu\neq\nu'.$$

[3] M. Born and E. Brody, Z. Physik 6, 132 (1921).
[4] W. Ludwig, J. Phys. Chem. Solids 4, 283 (1958).
[5] J. M. Keller and D. C. Wallace, Phys. Rev. 126, 1275 (1962).
[6] A. A. Maradudin, P. A. Flinn, and R. A. Coldwell-Horsfall, Ann. Phys. (N. Y.) 15, 337, 360 (1961).
[7] G. Leibfried and W. Ludwig, in Solid State Physics, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1961), Vol. 12, p. 275.
[8] See, for example, Refs. 2 and 7.

In (2.2) and (2.3), the Cartesian indices have been suppressed for abbreviation; each equality holds for any set of these indices. The coefficients $A_{\nu\nu}$, $B_{\nu\nu\nu}$, and $C_{\nu\nu\nu\nu}$ are defined, in terms of the other coefficients, by (2.2). Since the origin of coordinates can be taken at any lattice site in the unit cell, any of the subscripts ν can be reduced to zero by a uniform translation. Thus $A_{\nu,\nu'} = A_{0,\nu'-\nu}$, and similarly for B and C coefficients. These relations, combined with (2.3), specify the inversion symmetries

$$A_{0,\nu} = A_{0,-\nu},$$
$$B_{0,0,\nu} = -B_{0,0,-\nu}, C_{0,0,0,\nu} = C_{0,0,0,-\nu}. \quad (2.4)$$

Thus, when there is only one atom per unit cell, $B_{\nu\nu\nu} = 0$. It should be recognized that, when there is more than one atom per unit cell, if $\mathbf{r}_\nu$ is a lattice site, $\mathbf{r}_{-\nu} = -\mathbf{r}_\nu$ is not necessarily also a lattice site. In the reduction of (1.13) and (1.14) below, the final expressions have been cast into forms which contain only lattice site vectors.

In addition to the above symmetry relations, the combination of (2.1) and (2.3) shows that any potential energy coefficient remains unchanged if its Cartesian indices are interchanged in any way. This is a result of the restriction to two-body forces. Thus there are only 6 independent $A_{\nu\nu'}$ coefficients for fixed (ν,ν'), specified by different sets of Cartesian indices, 10 independent $B_{\nu\nu\nu'}$ for fixed (ν,ν'), and 15 independent $C_{\nu\nu\nu\nu'}$ for fixed (ν,ν').

Note added in proof. There is a restriction on the first equality in (2.3), namely $A_{\nu\nu'} = A_{\nu'\nu}$. This relation holds for any lattice when central forces are considered, and also for any force model when the lattice has a center of inversion symmetry (the center need not be a lattice point).

One Atom per Unit Cell

For the case of one atom per unit cell, the lattice has inversion symmetry, and the index ν becomes simply n, while ρ becomes i. With the aid of (2.2)–(2.4), and noting that for every $\mathbf{r}_n$ there is a $-\mathbf{r}_n$, it is possible to write

$$a_{\mathbf{k},ii'} = \sum'_n A_{0i,ni'}[\cos(\mathbf{k}\cdot\mathbf{r}_n)-1], \quad (2.5)$$

where the prime on $\sum'_n$ means to omit the term $n=0$ ($\mathbf{r}_n=0$). In addition, $A_{0i,ni'} = A_{0i',ni}$, so that $\mathbf{a}_\mathbf{k}$ is a real, symmetric matrix, and $\mathbf{a}_\mathbf{k} = \mathbf{a}_{-\mathbf{k}}$. $\lambda_\mathbf{k}$ is also real and symmetric, and equal to $\lambda_{-\mathbf{k}}$. This allows certain sums over the first Brillouin zone to be simplified:

$$\sum_\mathbf{k} \exp(i\mathbf{k}\cdot\mathbf{r}_n)\lambda_\mathbf{k} = \sum_\mathbf{k} \cos(\mathbf{k}\cdot\mathbf{r}_n)\lambda_\mathbf{k}. \quad (2.6)$$

With the aid of (1.15), (2.1)–(2.4), and (2.6), the equations for F_{3T} and F_{4T} can be simplified to the forms

$$F_{3T} = [N(KT)^2/12]$$
$$\times \sum_n \sum'_{n'} \sum'_{n''} \sum_{i\ldots i'} B_{0i,0i',n'i''}$$
$$\times B_{0i''',0i^{iv},n''i^v} G_{n,ii'''} H_{nn'n'',i'i^{iv}} H_{nn'n'',i''i^v}, \quad (2.7)$$

$$F_{4T} = [N(KT)^2/4] \sum'_n \sum_{i\ldots i'''} C_{0i,0i',ni'',ni'''}$$
$$\times J_{n,ii'}J_{n,i''i'''}, \quad (2.8)$$

where

$$G_{n,ii'} = N^{-1} \sum_\mathbf{k} \cos(\mathbf{k}\cdot\mathbf{r}_n)\lambda_{\mathbf{k},ii'}, \quad (2.9)$$

$$J_{n,ii'} = G_{0,ii'} - G_{n,ii'}, \quad (2.10)$$

$$H_{nn'n'',ii'} = G_{n,ii'} - G_{n+n',ii'} - G_{n+n'',ii'}$$
$$+ G_{n+n'+n'',ii'}. \quad (2.11)$$

$\mathbf{G}_n$, $\mathbf{J}_n$, and $\mathbf{H}_{nn'n''}$ are real, symmetric matrix functions.

Two Atoms per Unit Cell

For a lattice with two atoms per unit cell, the $\mathbf{a}_\mathbf{k}$ matrices are of order 6. The symmetry properties of these matrices are conveniently discussed in terms of four submatrices of order 3. Suppressing the index $\mathbf{k}$,

$$\mathbf{a} = \begin{pmatrix} \gamma_1 & \kappa \\ \kappa^\dagger & \gamma_2 \end{pmatrix}, \quad \text{for each } \mathbf{k}.$$

These four matrices are each defined by (1.7); the elements of each submatrix are labeled by Cartesian indices. If j and j' represent the two lattice sites per unit cell, $j \neq j'$, then a consistent choice is

$$\mathbf{a}_{jj} = \gamma_1, \quad \mathbf{a}_{j'j'} = \gamma_2, \quad \mathbf{a}_{jj'} = \kappa.$$

Now, for simplicity, the remaining derivation will be carried out for the case where all two-body interactions are represented by a single central-force form. The general case is quite analogous. Thus, for central forces, $A_{nji,n'ji'} = A_{nj'i,n'j'i'}$, and hence $\mathbf{a}_{jj} = \mathbf{a}_{j'j'}$. Furthermore, since $A_{\nu i,\nu' i'} = A_{\nu' i',\nu' i}$, $\mathbf{a}_{jj}$ and $\mathbf{a}_{j'j'}$ are symmetric matrices. This fact, in conjunction with the Hermiticity of $\mathbf{a}$, requires that $\mathbf{a}_{jj}$ be real and that $\mathbf{a}_{jj'} = \mathbf{a}_{j'j}^*$. Thus

$$\mathbf{a} = \begin{pmatrix} \gamma & \kappa \\ \kappa^* & \gamma \end{pmatrix}, \quad \text{for each } \mathbf{k}, \quad (2.12)$$

where

$$\gamma_{\mathbf{k},ii'} = \sum'_n A_{0ji,nji'}[\cos(\mathbf{k}\cdot\mathbf{r}_n)-1]$$
$$- \sum_n A_{0ji,nj'i'}, \quad j \neq j'; \quad (2.13)$$

$$\kappa_{\mathbf{k},ii'} = \exp[-i\mathbf{k}\cdot(\mathbf{r}_j - \mathbf{r}_{j'})] \sum_n A_{0ji,nj'i'}$$
$$\times \exp(i\mathbf{k}\cdot\mathbf{r}_n), \quad j \neq j'. \quad (2.14)$$

Since $\gamma_\mathbf{k}$ is real symmetric and $\kappa_\mathbf{k}$ is complex symmetric, there are only 18 independent elements for each $\mathbf{a}_\mathbf{k}$ matrix. The $\lambda_\mathbf{k}$ matrices can be similarly defined in terms of four submatrices of order 3, and the symmetries of these submatrices follow from the symmetries of $\gamma_\mathbf{k}$ and $\kappa_\mathbf{k}$ and the Hermiticity of $\lambda_\mathbf{k}$:

$$\lambda_\mathbf{k} = \begin{pmatrix} \eta_\mathbf{k} & \zeta_\mathbf{k} \\ \zeta_\mathbf{k}^* & \eta_\mathbf{k}^* \end{pmatrix}, \quad (2.15)$$

where $\eta_\mathbf{k}$ is Hermitian and $\zeta_\mathbf{k}$ is complex symmetric,

The treatment of (1.13) and (1.14) for the case of two atoms per unit cell is a great deal more complicated than for one atom per unit cell. This is because the elements of the λ_k, the exponential factors, and the B or C coefficients are all coupled in a complicated way through the indices j, j', $\cdots$. It was found that the greatest reduction, for computational purposes, could be obtained by grouping together all terms corresponding to a given set of j indices. This gives rise to 16 sets of terms in F_{4T}, and 64 sets of terms in F_{3T}. After lengthy algebraic simplification, it is then possible to recombine the various sets of terms to a large degree. This procedure leads to a description in terms of the submatrices η_k and ζ_k. More specifically, if the origin of coordinates is taken at a j site, then $r_j = 0$ and $r_{j'}$ is the basis vector. All lattice site vectors r_ν are either vectors to primitive lattice points, r_{nj}, or vectors to basis points, $r_{nj'}$. The dependence of F_{3T} and F_{4T} upon the λ_k is then expressible in terms of the matrix functions G_ν:

$$G_{\nu,ii'} = N^{-1} \sum_k \exp(i\mathbf{k}\cdot\mathbf{r}_\nu)\eta_{k,ii'}, \quad \text{if } \mathbf{r}_\nu \text{ is a}$$
$$\text{primitive lattice point;}$$
$$G_{\nu,ii'} = N^{-1} \sum_k \exp(i\mathbf{k}\cdot\mathbf{r}_\nu)\zeta_{k,ii'}^*, \quad \text{if } \mathbf{r}_\nu \text{ is a} \qquad (2.16)$$
$$\text{basis point.}$$

Because of the general relation (1.9), $\eta_k = \eta_{-k}^*$ and $\zeta_k = \zeta_{-k}^*$; thus the G_ν are all real. In addition, $G_\nu = \tilde{G}_{-\nu}$ if r_ν is a primitive lattice point, whereas G_ν is symmetric if r_ν is a basis point.

With the aid of (2.16), and all the symmetry properties of the C coefficients and the λ_k matrices, F_{4T} is found to consist of two sums of the form

$$[N(KT)^2/2] \sum_\nu{}' \sum_{ii'i''i'''} C_{0i,0i',\nu i'',\nu i'''}$$
$$\times J_{\nu,ii'} J_{\nu,i''i'''}; \qquad (2.17)$$

Sum 1. $\sum'_\nu$ is over primitive lattice points,

$$J_\nu = G_0 - \tfrac{1}{2}[G_\nu + G_{-\nu}];$$

Sum 2. $\sum'_\nu$ is over basis points,

$$J_\nu = G_0 - G_\nu.$$

F_{3T} is found to consist of six sums of the form

$$Q[N(KT)^2/6] \sum_\nu \sum'_{\nu'} \sum'_{\nu''} \sum_{i\cdots i^v} B_{0i,0i',\nu'i''}$$
$$\times B_{0i''',0i^{iv},\nu''i^v} G_{\nu,ii'''} H_{\nu\nu'\nu'',i'i^{iv}} H_{\nu\nu'\nu'',i''i^v}; \qquad (2.18)$$

Sum 1. $Q = -1$; ν, ν', ν'' are primitive points,

$$\mathbf{H}_{\nu\nu'\nu''} = \mathbf{G}_\nu - \mathbf{G}_{\nu+\nu'} - \mathbf{G}_{\nu-\nu''} + \mathbf{G}_{\nu+\nu'-\nu''};$$

Sum 2. $Q = -2$; ν, ν' primitive, ν'' basis,

$$\mathbf{H}_{\nu\nu'\nu''} = \mathbf{G}_\nu - \mathbf{G}_{\nu+\nu'} - \mathbf{G}_{\nu''-\nu} + \mathbf{G}_{\nu''-\nu-\nu'};$$

Sum 3. $Q = -1$; ν primitive, ν', ν'' basis,

$$\mathbf{H}_{\nu\nu'\nu''} \text{ same as in sum 2;}$$

Sum 4. $Q = +1$; ν basis, ν', ν'' primitive,

$$\mathbf{H}_{\nu\nu'\nu''} = \mathbf{G}_\nu - \mathbf{G}_{\nu+\nu'} - \mathbf{G}_{\nu+\nu''} + \mathbf{G}_{\nu+\nu'+\nu''};$$

Sum 5. $Q = +2$; ν, ν'' basis, ν' primitive,

$$\mathbf{H}_{\nu\nu'\nu''} = \mathbf{G}_\nu - \mathbf{G}_{\nu-\nu'} - \mathbf{G}_{\nu''-\nu} + \mathbf{G}_{\nu''+\nu'-\nu};$$

Sum 6. $Q = +1$; ν, ν', ν'' basis points,

$$\mathbf{H}_{\nu\nu'\nu''} \text{ same as in sum 5.}$$

Although this formulation of F_{3T} is admittedly cumbersome, it represents a computational problem which is quite feasible. A further computational aid, namely, the transformation of all $\mathbf{a}_k$ matrices to real, symmetric forms, is outlined in the Appendix.

III. RESULTS FOR CENTRAL FORCES

The restriction to central forces affords very little further simplification of the general formulas of Sec. II for F_{3T} and F_{4T}. However, a central-force model does give rise to a simple description of the potential energy coefficients in terms of the derivatives of the central potential functions. Certain of these relations have been given previously for special cases[4-7]; it is possible to give a general set of relations. If $\psi_{\nu\nu'}(r^2)$ is the central potential between two ions ν and ν' a distance r apart, then the total potential of the crystal is

$$U = \tfrac{1}{2} \sum_{\nu\nu'} \psi_{\nu\nu'}(|\mathbf{r}_\nu + \mathbf{u}_\nu - \mathbf{r}_{\nu'} - \mathbf{u}_{\nu'}|^2), \qquad (3.1)$$

where it is understood that the functional form of $\psi_{\nu\nu'}$ may depend upon the types of ions which are coupled, i.e., upon the indices j, j'. Each $\psi_{\nu\nu'}$ may be expanded in a Taylor series about the equilibrium distance between the ions ν and ν'. Let $\phi_{\nu\nu'}$ represent $\psi_{\nu\nu'}$ evaluated at equilibrium, i.e., $\phi_{\nu\nu'} = \psi_{\nu\nu'}(|\mathbf{r}_\nu - \mathbf{r}_{\nu'}|^2)$, and let $\phi'_{\nu\nu'}$ represent the first derivative of $\psi_{\nu\nu'}(r^2)$, with respect to r^2, evaluated at equilibrium, and so forth for higher derivatives. Then

$$\psi_{\nu\nu'}(|\mathbf{r}_\nu + \mathbf{u}_\nu - \mathbf{r}_{\nu'} - \mathbf{u}_{\nu'}|^2) = \phi_{\nu\nu'} + \sigma_{\nu\nu'}\phi'_{\nu\nu'}$$
$$+ \tfrac{1}{2}(\sigma_{\nu\nu'})^2\phi''_{\nu\nu'} + \cdots, \qquad (3.2)$$

where

$$\sigma_{\nu\nu'} = 2(\mathbf{r}_\nu - \mathbf{r}_{\nu'})\cdot(\mathbf{u}_\nu - \mathbf{u}_{\nu'}) + |\mathbf{u}_\nu - \mathbf{u}_{\nu'}|^2. \qquad (3.3)$$

Equation (3.2) is now used in (3.1), with terms up to fourth order in displacements being kept. The resulting expression for U is then compared with the general potential energy expansion of (1.2)–(1.4), with like powers of the displacements being equated. The results for the A, B, and C coefficients are, for $\nu \neq 0$,

$$A_{0i,\nu i'} = -2[\phi'_{0\nu}\delta_{ii'} + 2\phi''_{0\nu}r_{\nu i}r_{\nu i'}],$$

$$B_{0i,0i',\nu i''} = 4[\phi''_{0\nu}(r_{\nu i}\delta_{i'i''} + r_{\nu i'}\delta_{ii''} + r_{\nu i''}\delta_{ii'})$$
$$+ 2\phi'''_{0\nu}r_{\nu i}r_{\nu i'}r_{\nu i''}],$$

$$C_{0i,0i',0i'',\nu i'''} = -4[\phi''_{0\nu}(\delta_{ii'}\delta_{i''i'''} + \delta_{ii''}\delta_{i'i'''}$$
$$+ \delta_{ii'''}\delta_{i'i''}) + 2\phi'''_{0\nu}(r_{\nu i}r_{\nu i'}\delta_{i''i'''} \qquad (3.4)$$
$$+ r_{\nu i}r_{\nu i''}\delta_{i'i'''} + r_{\nu i}r_{\nu i'''}\delta_{i'i''}$$
$$+ r_{\nu i'}r_{\nu i''}\delta_{ii'''} + r_{\nu i'}r_{\nu i'''}\delta_{ii''}$$
$$+ r_{\nu i''}r_{\nu i'''}\delta_{ii'})$$
$$+ 4\phi^{iv}_{0\nu}r_{\nu i}r_{\nu i'}r_{\nu i''}r_{\nu i'''}].$$

Here $\delta_{ii'}$ is the usual Kronecker delta, and the origin of coordinates may be taken at any lattice site. All other two-body central-force coefficients can be obtained from these expressions, together with the symmetry relations of Sec. II. It should be pointed out that, although there has been no particular restriction to a Cartesian coordinate system in the development of Secs. I and II, Eqs. (3.4) have been obtained strictly for an orthogonal coordinate system.

There are certain useful relations between different coefficients as defined by (3.4). These can be summarized by two rules, which show how each coefficient is transformed under a given transformation of $\mathbf{r}_\nu$.

(a) If two Cartesian coordinates of $\mathbf{r}_\nu$ are interchanged, the corresponding Cartesian indices are interchanged on all coefficients.

(b) If the sign of one Cartesian coordinate of $\mathbf{r}_\nu$ is changed, then each coefficient is multiplied by -1 for each Cartesian index corresponding to that particular coordinate.

These relations are particularly valuable for a lattice with cubic symmetry, since the specified transformations of $\mathbf{r}_\nu$ are elements of the cubic point group. These rules can be applied repeatedly.

For all numerical calculations in the present work, the central potentials have been represented by the Lennard-Jones form

$$\psi(r^2) = (A_\alpha/r^\alpha) - (B_\beta/r^\beta), \qquad (3.5)$$

where A_α, B_β, α, and β are arbitrary positive constants, and $\alpha > \beta$. Calculations have been carried out for several sets of α and β for fcc and hcp lattices. The equilibrium positions of the ions in the crystal are determined by the crystal symmetry and by the nearest-neighbor distance ϵ. The nearest-neighbor distance has been chosen as that which minimizes U_0, the crystal potential energy when all the ions are at rest and located at symmetry-determined positions. This procedure leads to the equations, valid for one or two atoms per unit cell,

$$U_0(\epsilon) = -(NJ)D, \qquad (3.6)$$

$$D = (\alpha-\beta)A_\alpha S_\alpha/2\beta\epsilon^\alpha = (\alpha-\beta)B_\beta S_\beta/2\alpha\epsilon^\beta, \qquad (3.7)$$

where

$$S_\alpha = \sum_\nu [\epsilon/|\mathbf{r}_\nu|]^\alpha. \qquad (3.8)$$

If zero-point effects are neglected, D represents the binding energy per atom for the model under consideration. The lattice potential constants, S_α, have been tabulated for fcc[9] and hcp[10]; they were recalculated to greater accuracy in the present work. In addition,

[9] J. E. Jones and A. E. Ingham, Proc. Roy. Soc. (London) **A107**, 636 (1925).
[10] T. H. K. Barron and C. Domb, Proc. Roy. Soc. (London) **A227**, 447 (1955).

for the Lennard-Jones model, there results

$$\phi'_{0\nu} = [\alpha\beta D/\epsilon^2(\alpha-\beta)][S_\beta^{-1}(\bar{r}_\nu)^{-(\beta+2)} \\ - S_\alpha^{-1}(\bar{r}_\nu)^{-(\alpha+2)}],$$

$$\phi''_{0\nu} = [\alpha\beta D/2\epsilon^4(\alpha-\beta)][(\alpha+2)S_\alpha^{-1}(\bar{r}_\nu)^{-(\alpha+4)} \\ - (\beta+2)S_\beta^{-1}(\bar{r}_\nu)^{-(\beta+4)}],$$

$$\phi'''_{0\nu} = [\alpha\beta D/4\epsilon^6(\alpha-\beta)] \\ \times[(\beta+2)(\beta+4)S_\beta^{-1}(\bar{r}_\nu)^{-(\beta+6)} \\ - (\alpha+2)(\alpha+4)S_\alpha^{-1}(\bar{r}_\nu)^{-(\alpha+6)}], \qquad (3.9)$$

$$\phi^{iv}_{0\nu} = [\alpha\beta D/8\epsilon^8(\alpha-\beta)] \\ \times[(\alpha+2)(\alpha+4)(\alpha+6)S_\alpha^{-1}(\bar{r}_\nu)^{-(\alpha+8)} \\ - (\beta+2)(\beta+4)(\beta+6)S_\beta^{-1}(\bar{r}_\nu)^{-(\beta+8)}].$$

Here $\bar{r}_\nu$ is the dimensionless "distance" $[|\mathbf{r}_\nu|/\epsilon]$.

Finally, all calculations were carried out in terms of dimensionless quantities, which are indicated by a superscript bar. For example,

$$\bar{\phi}_{0\nu} = (1/D)\phi_{0\nu}, \qquad \bar{\phi}'_{0\nu} = (\epsilon^2/D)\phi'_{0\nu}, \quad \text{etc.};$$

$$\bar{A}_{\nu\nu'} = (\epsilon^2/D)A_{\nu\nu'}, \qquad \bar{B}_{\nu\nu\nu'} = (\epsilon^3/D)B_{\nu\nu\nu'},$$

$$\bar{C}_{\nu\nu\nu\nu'} = (\epsilon^4/D)C_{\nu\nu\nu\nu'}; \qquad (3.10)$$

$$\bar{F}_{3T} = [D/(KT)^2](F_{3T}/JN),$$

$$\bar{F}_{4T} = [D/(KT)^2](F_{4T}/JN).$$

$\bar{F}_{3T}$ and $\bar{F}_{4T}$ are the dimensionless anharmonic free-energy contributions per atom of the crystal. Upon transforming to dimensionless quantities, the explicit ϵ dependence disappears from $\bar{F}_{3T}$ and $\bar{F}_{4T}$.

Face-Centered Cubic Lattice

The lattice points are given by

$$\mathbf{r}_n = (\epsilon/\sqrt{2})(n_1\mathbf{x} + n_2\mathbf{y} + n_3\mathbf{z}), \qquad (3.11)$$

where $\mathbf{x}$, $\mathbf{y}$, and $\mathbf{z}$ are unit Cartesian vectors, and where n_1, n_2, and n_3 take on all integral values (including zero) subject to the condition $(n_1+n_2+n_3)$ is even (or zero). The dynamical matrices were first computed numerically for all the chosen $\mathbf{k}$ vectors in the irreducible portion of the first zone (see below), and stored on magnetic tape. In carrying out the sums over lattice points, all points within a large sphere were taken. In addition, a remainder was added to the diagonal elements of the matrices, to account for the points lying outside the sphere; no remainder was necessary for off-diagonal elements. The radius of the sphere, and the remainder, depended upon the parameters α and β. Exhaustive convergence studies were carried out in order to determine the accuracy of the sums over lattice points. The six independent elements of each matrix were computed within an error of 0.1% of the smallest eigenvalue.

Since the lattice has the full cubic point group, it is only necessary to compute $\mathbf{a}_k$ for $\mathbf{k}$ lying in 1/48 of the first zone. The wave vectors, along with the restrictions

to an appropriate portion of the zone, are

$$\mathbf{k}_p = (\sqrt{2}\pi/\epsilon P)(p_1\mathbf{x} + p_2\mathbf{y} + p_3\mathbf{z}); \qquad (3.12)$$

$$0 \leq p_3 \leq P,$$

$$0 \leq p_2 \leq p_2', \quad p_2' = \text{minimum of } (p_3, \tfrac{3}{2}P - p_3),$$

$$0 \leq p_1 \leq p_1', \quad p_1' = \text{minimum of } (p_2, \tfrac{3}{2}P - p_3 - p_2).$$

Here P is taken to be a positive number, and p_1, p_2, and p_3 take on all integral values, subject to the conditions listed in (3.12). Thus, a simple cubic lattice of points in $\mathbf{k}$ space was generated.

In all the calculations, sums over the first zone were reduced to sums over the 1/48 of the zone defined by (3.12). In such sums over 1/48 of the zone, each contribution was multiplied by a weighting factor which depended upon the position of $\mathbf{k}$. The weighting factors were chosen so that each point within the zone would be counted exactly once, and each point on the surface exactly one-half, if a sum were carried out over all 48 equivalent sets of points. The point $\mathbf{k}=0$ was not counted in summing over the zone.

Studies of the accuracy of sums over the zone were carried out by taking different values of P. As was expected, the accuracy of such sums was essentially independent of the parameters α and β in the Lennard-Jones potential. It is particularly simple to find the average over $\mathbf{k}$ of the traces of the $\mathbf{a}_\mathbf{k}$ matrices, since these traces have the full 48-fold symmetry. It is also possible to calculate this average separately, in terms of the lattice potential constants [see Eq. (4.9)]. For $P=16$, corresponding to 504 points in 1/48 of the zone, or to 16 431 distinct points in the entire zone, the average of the traces is accurate to 0.1%; without the weighting factors the same sum is only accurate to 2%.

The calculation of the $\mathbf{G}_n$ matrices, in terms of a sum over 1/48 of the zone, requires a knowledge of the symmetry in $\mathbf{k}$ space of all the elements of the $\mathbf{a}_\mathbf{k}$. These symmetries are easily found with the aid of the lattice symmetry and the relations between different A coefficients, as given by rules (a) and (b) previously stated, and are valid for any primitive cubic lattice.

(c) If two Cartesian coordinates of $\mathbf{k}$ are interchanged, the corresponding Cartesian indices are interchanged on all elements of $\mathbf{a}_\mathbf{k}$.

(d) If the sign of one Cartesian coordinate of $\mathbf{k}$ is changed, then each element of $\mathbf{a}_\mathbf{k}$ is multiplied by -1 for each Cartesian index corresponding to that particular coordinate.

These rules also hold for $\boldsymbol{\lambda}_\mathbf{k}$ in place of $\mathbf{a}_\mathbf{k}$, as a direct consequence of the definition $\boldsymbol{\lambda}_\mathbf{k} = \mathbf{a}_\mathbf{k}^{-1}$. Again the operations can be applied repeatedly. The final formulas for the elements of $\mathbf{G}_n$ are quite simple for computational purposes, but need not be given here. For $P=16$, the elements of all $\mathbf{G}_n$ are accurate to 1.5%.

Rules (c) and (d) lead to relations between the elements of different $\mathbf{G}_n$ which are identical to the relations between the components of different A coefficients, as given by rules (a) and (b) above. A final simplification of (2.7) and (2.8) is possible with the aid of these relations between different $\mathbf{G}_n$ matrices, and the similar relations between different B and C coefficients. It can be shown that the contribution of each term in the $\sum_n$ of (2.7), and the $\sum'_n$ of (2.8), is the same for all points $\mathbf{r}_n$ which are obtained from one another by operations of the cubic point group. Thus, in both F_{3T} and F_{4T}, this outer sum can be obtained by taking only one lattice point in each shell of points which are related by cubic point group operations, and multiplying by the number of points in the shell.

$\bar{F}_{3T}$ and $\bar{F}_{4T}$ were calculated by taking nearest neighbors only, and also nearest plus next neighbors, in the sums over lattice points in (2.7) and (2.8). The difference between the two calculations is represented by Δ_3 and Δ_4, respectively, where

$$\Delta = \frac{(\text{nearest plus next}) - (\text{nearest})}{(\text{nearest plus next})}.$$

The results for nearest plus next neighbors, along with the appropriate values of Δ, are given in Table I. The

TABLE I. Anharmonic contributions to the high-temperature free energy for the face-centered cubic lattice.

α	β	$\bar{F}_{3T}$	Δ_3	$\bar{F}_{4T}$	Δ_4
12	10	-1.82	-0.003	3.44	-0.002
12	8	-1.92	-0.003	3.53	-0.001
12	6	-2.09	-0.004	3.75	0.000
12	4	-2.44	-0.005	4.27	0.003
10	8	-1.92	-0.004	3.35	0.000
10	6	-2.05	-0.005	3.42	0.002
8	6	-2.06	-0.005	3.11	0.007
6	4	-2.34	-0.008	2.57	0.038

tabulated values of $\bar{F}_{3T}$ and $\bar{F}_{4T}$ represent the Lennard-Jones model chosen to an over-all accuracy of at least 2%. All final calculations were carried out with $P=16$. For one case of α and β and for nearest neighbors only, the calculation of $\bar{F}_{3T}$ required 14 min of computer time, while $\bar{F}_{4T}$ required less than 1 min.

Hexagonal Close-Packed Lattice

The primitive lattice points are given by

$$\mathbf{r}_n = \epsilon(n_1\mathbf{b}_1 + n_2\mathbf{b}_2 + n_3\mathbf{b}_3), \qquad (3.13)$$

and the basis vector is $\epsilon(\tfrac{1}{3}\mathbf{b}_1 + \tfrac{2}{3}\mathbf{b}_2 + \tfrac{1}{2}\mathbf{b}_3)$, where $\mathbf{b}_1$, $\mathbf{b}_2$, and $(\tfrac{3}{8})^{1/2}\mathbf{b}_3$ are unit vectors in a simple hexagonal coordinate system, and n_1, n_2, and n_3 take on all integral values. Since all the potential energy coefficients have been defined according to their Cartesian components, the calculations were carried out entirely in Cartesian coordinates. These are defined by

$$\mathbf{x} = (\mathbf{b}_1 + \mathbf{b}_2), \quad \mathbf{y} = (3)^{-1/2}(\mathbf{b}_2 - \mathbf{b}_1), \quad \mathbf{z} = (\tfrac{3}{8})^{1/2}\mathbf{b}_3. \qquad (3.14)$$

It was necessary to compute dynamical matrices for $\mathbf{k}$ lying in $\frac{1}{8}$ of the first zone, since there is only 8-fold symmetry in $\mathbf{k}$ space for all the elements of these matrices, even though the eigenvalues have 24-fold symmetry. This reduction in symmetry results from the specification of the $\mathbf{a}_k$ matrix elements in terms of Cartesian indices, but this complication is more than compensated by the other advantages of Cartesian coordinates. The 18 independent elements of each $\mathbf{a}_k$ matrix were computed, again to 0.1% of the smallest eigenvalue, as determined by numerical convergence studies, and stored on magnetic tape. Again remainders were added to the diagonal elements to correct for slow convergence of these particular sums.

If the unit vectors defining the simple hexagonal reciprocal lattice are $(\frac{3}{4})^{1/2}\mathbf{c}_1$, $(\frac{3}{4})^{1/2}\mathbf{c}_2$, and $(8/3)^{1/2}\mathbf{c}_3$, then the wave vectors, along with restrictions to $\frac{1}{8}$ of the zone, are

$$\mathbf{k}_p = (\pi/P\epsilon)(p_1\mathbf{c}_1 + p_2\mathbf{c}_2 + p_3\mathbf{c}_3),\qquad (3.15)$$

$$0 \leq p_3 \leq P, \quad 0 \leq p_2 \leq \tfrac{3}{4}P, \quad p_1' \leq p_1 \leq p_1'',$$

$p_1' =$ algebraic maximum of $(-p_2, p_2 - 2P)$,

$p_1'' =$ algebraic minimum of $(p_2, 2P - 2p_2)$.

P is taken to be a positive number, and p_1, p_2, and p_3 take on all integral values, thus generating a simple hexagonal lattice of points in $\mathbf{k}$ space. The point $\mathbf{k}=0$ was not counted. The eight equivalent portions of the first zone are related by the eight possible sign combinations of the Cartesian components k_x, k_y, and k_z of $\mathbf{k}$. Weighting factors were used in all sums over $\mathbf{k}$, and the accuracy of such sums was studied by taking different values of P. For $P=8$, corresponding to 674 points in $\frac{1}{8}$ of the zone, or to 4110 distinct points in the entire zone, the average of the traces of the dynamical matrices is accurate to 0.1%. Without weighting factors, the same sum is accurate to 0.3%.

For the calculation of the $\mathbf{G}_\nu$ matrix functions for the hcp lattice, the $\mathbf{a}_k$ matrices were first transformed to real, symmetric form, this form was inverted, and the submatrices $\boldsymbol{\eta}_k$ and $\boldsymbol{\zeta}_k$ of (2.15) were calculated. This procedure is outlined in the Appendix. In addition, the sums over the first zone were replaced by sums over 1/8 of the zone, with the aid of the following rules.

(e) If the sign of k_x (or k_z) is changed, then each element of $\mathbf{a}_k$ is multiplied by -1 for each Cartesian index x (or z).

(f) If the sign of k_y is changed, then the complex conjugate of $\mathbf{a}_k$ is taken and each element is multiplied by -1 for each Cartesian index y.

These rules also hold for $\boldsymbol{\lambda}_k$ in place of $\mathbf{a}_k$.

As for the fcc lattice, there are some relations between the components of different $\mathbf{G}_\nu$, but these relations are not sufficient to lead to very much com-

TABLE II. Anharmonic contributions to the high-temperature free energy for the hexagonal close-packed lattice.

α	β	$\bar{F}_{3T}$	$\bar{F}_{4T}$	Δ_4
12	10	-1.88	3.54	-0.002
12	8	-1.98	3.63	-0.001
12	6	-2.16	3.87	0.000
12	4	-2.52	4.41	0.003
10	8	-1.98	3.45	0.000
10	6	-2.13	3.54	0.002
8	6	-2.13	3.22	0.006
6	4	-2.45	2.67	0.031

putational simplification. In calculating $\bar{F}_{4T}$, all sums over lattice points in (2.17) were taken to nearest neighbors only, and also to nearest plus next. The results for nearest-plus-next neighbors are listed in Table II, along with values of Δ_4, representing the difference between the two calculations, as for the fcc above. The tabulated results are accurate to 2%. In calculating $\bar{F}_{3T}$, all sums were taken to nearest neighbors only, and then the calculation was repeated with the outer sum in (2.18) extended to third neighbors. The difference between these two calculations was always less than 0.7%. Note that this outer sum arises from the $\delta(\mathbf{k}+\mathbf{k}'+\mathbf{k}'')$ function in F_3. Table II lists the results of the nearest-neighbor-only calculation of $\bar{F}_{3T}$; these values are accurate to 3%. All final calculations were carried out with $P=8$. For one case of α and β and for nearest neighbors only, the calculation of $\bar{F}_{3T}$ required 15 min of computer time, while $\bar{F}_{4T}$ required 1 min.

IV. APPROXIMATIONS

Because of the complexity of the expressions for F_3 and F_4, and the attendant difficulty of accurate calculations, it is highly desirable to develop some approximations. In this section, a particularly simple approximation is discussed, and evaluated for the same models for which the accurate calculations have been carried out. In addition, comparisons are made with other approximations which have been published.

First of all, it is noted that the general expressions for F_{3T} and F_{4T}, as given by (1.13) and (1.14), respectively, are independent of the masses of the atoms,[11] and depend only upon the potential energy coefficients and the lattice structure. This suggests the use of an approximation which can be defined independently of the masses M_j, in contrast to the two approximations suggested by Leibfried and Ludwig.[12] One possibility is to replace all $\mathbf{a}_k$ matrices by a multiple of the unit matrix, since the $\mathbf{a}_k$ defined by (1.7) do not depend on

[11] There can be implicit dependence of F_{3T} and F_{4T} upon the masses of the atoms, insofar as the nearest-neighbor distance can depend upon the masses when the total lattice free energy, including vibrations, is minimized to determine ϵ. Such dependence does not affect the argument here.

[12] See Ref. 7, p. 361.

the masses. For this approximation, let

$$a_{k,\rho\rho'} = \Omega\delta_{\rho\rho'},$$

$$\Omega = (3JN)^{-1}\sum_k \sum_\rho a_{k,\rho\rho} = (3J)^{-1}\sum_\rho A_{n\rho,n\rho}. \quad (4.1)$$

Thus, Ω is the average over k of the traces of the dynamical matrices, divided by the order of the matrices. The calculation of Ω for any force model is quite simple; with the aid of (2.2) the sum can be transformed to the form

$$\Omega = -(3J)^{-1}\sum_{ji}\sum'_{nj'} A_{0ji,nj'i}, \quad (4.2)$$

where the prime on $\sum'_{nj'}$ means to omit the term $(0,j)$. With the approximation (4.1), F_{3T} and F_{4T} become

$$f_{3T} = -[N(KT)^2/12\Omega^3]\sum_{nn',\rho\rho'\rho''}(B_{0\rho,n\rho',n'\rho''})^2, \quad (4.3)$$

$$f_{4T} = [N(KT)^2/8\Omega^2]\sum_{n,\rho\rho'}C_{0\rho,0\rho,n\rho',n\rho'}. \quad (4.4)$$

Here f_{3T} denotes an approximation to F_{3T}, and similarly for f_{4T}. In obtaining f_{3T}, the $\delta(k+k'+k'')$ function has been treated exactly, with the aid of (1.15). When two-body forces are considered, these expressions can be reduced further, as for the general calculations of Sec. II. The results can be combined for the cases of one or two atoms per unit cell ($J=1$ or 2):

$$f_{3T} = -[NJ(KT)^2/4\Omega^3]\left[\sum'_\nu \sum_{ii'i''}(B_{0i,0i',\nu i''})^2\right.$$
$$\left. +\tfrac{1}{3}\sum_{ii'i''}(B_{0i,0i',0i''})^2\right]; \quad (4.5)$$

$$f_{4T} = [NJ(KT)^2/4\Omega^2]\sum'_\nu \sum_{ii'}C_{0i,0i,\nu i',\nu i'}. \quad (4.6)$$

Here the contribution to each term in the $\sum'_\nu$ is the same for all points r_ν which are obtained from one another by operations of the cubic point group. For one atom per unit cell, the terms $B_{0i,0i',0i''}$ vanish.

Finally, if the restriction to central forces is made, the approximations can be expressed in terms of the derivatives of the central potential function. For the range of forces considered in the present work, the sums over lattice points in (4.5) and (4.6) converge very rapidly with increasing distance from the origin. Therefore, the explicit expressions are given for nearest

neighbors only. For the fcc and hcp lattices,

$$f_{3T} = -JN(KT)^2[48\epsilon^2/\Omega^3]$$
$$\times\{[15(\phi'')^2+12\phi''\phi'''\epsilon^2+4(\phi''')^2\epsilon^4]$$
$$+[(1/27)(\phi''')^2\epsilon^4 \text{ for hcp}]\}; \quad (4.7)$$

$$f_{4T} = JN(KT)^2[12/\Omega^2][15\phi''+20\phi'''\epsilon^2+4\phi^{iv}\epsilon^4]. \quad (4.8)$$

Here all ϕ'', ϕ''', and ϕ^{iv} are to be evaluated at the nearest-neighbor distance. The term $(1/27)(\phi''')^2\epsilon^4$ in (4.7) represents the term $\tfrac{1}{3}\sum_{ii'i''}(B_{0i,0i',0i''})^2$ in (4.5), and is to be included only for the hcp lattice.

Numerical evaluation of (4.7) and (4.8) has been carried out for the Lennard-Jones central potential model of Sec. III. For this model, Ω is given by

$$\Omega = [2\alpha\beta D/3\epsilon^2(\alpha-\beta)]$$
$$\alpha\times[(-1)S_\alpha^{-1}S_{\alpha+2}-(\beta-1)S_\beta^{-1}S_{\beta+2}]. \quad (4.9)$$

Equation (4.9) is valid for any lattice with one or two atoms per unit cell, subject to the choice of ϵ as that which minimizes U_0, as discussed in Sec. III. Equations (4.7) and (4.8) were transformed to dimensionless quantities, according to (3.10) and with

$$\bar{\Omega} = (\epsilon^2/D)\Omega,$$
$$\bar{f}_{3T} = (f_{3T}/JN)[D/(KT)^2], \quad (4.10)$$

and similarly for $\bar{f}_{4T}$. The explicit ϵ-dependence again disappears from $\bar{f}_{3T}$ and $\bar{f}_{4T}$. The results of these calculations for the fcc lattice are listed in Table III. The next-nearest neighbor contributions to the sums over lattice points in (4.5) and (4.6) were also calculated for the fcc lattice. These contributions are significantly smaller than the additional contributions in the accurate calculations, when the sums over lattice points are extended to next-nearest neighbors. For $\bar{f}_{3T}$, the next-nearest neighbor contribution was always less than 0.1%; for $\bar{f}_{4T}$ this contribution ranged from 0.1% for $\alpha=12$, $\beta=10$ to 1% for $\alpha=6$, $\beta=4$.

Table III also lists the errors of the approximation, as compared to the accurate values of Table I, in the

TABLE III. Approximate calculations of the high-temperature anharmonic free energy for the face-centered cubic lattice. Except where otherwise indicated, columns 3–8 represent the results of the present approximation, Eqs. (4.7)–(4.9). The last two columns represent the results of Ref. 6, as expressed by Eqs. (4.12)–(4.14).

α	β	$\bar{\Omega}$	$\bar{f}_{3T}$	$\bar{f}_{4T}$	$\delta\bar{f}_{3T}$	$\delta\bar{f}_{4T}$	$\delta(\bar{f}_{3T}+\bar{f}_{4T})$	$\bar{f}_{3T}$	$\bar{f}_{4T}$
12	10	82.6	−1.42	3.62	0.22	−0.05	−0.36	−1.52	4.22
12	8	67.2	−1.46	3.69	0.24	−0.05	−0.39	−1.48	4.25
12	6	52.0	−1.54	3.87	0.26	−0.03	−0.40	−1.43	4.31
12	6	⋯	−1.21[a]	3.07[a]	0.42[a]	−0.18[a]	−0.12[a]	⋯	⋯
12	4	36.9	−1.69	4.27	0.31	0.00	−0.41	−1.34	4.43
10	8	57.0	−1.44	3.49	0.25	−0.04	−0.43	−1.38	4.01
10	6	44.4	−1.48	3.52	0.28	−0.03	−0.49	−1.28	3.90
10	4	31.8	−1.56	3.67	⋯	⋯	⋯	−1.13	3.80
8	6	36.8	−1.42	3.16	0.31	−0.02	−0.66	−1.11	3.47
8	4	26.8	−1.44	3.06	⋯	⋯	⋯	−0.93	3.16
6	4	21.7	−1.32	2.41	0.44	0.06	−3.7	−0.72	2.52

[a] The approximate calculation of Ref. 5.

form of $\delta \bar{f}_{3T}$, $\delta \bar{f}_{4T}$, and $\delta(\bar{f}_{3T}+\bar{f}_{4T})$, where

$$\delta \bar{f}_{3T}=(\bar{F}_{3T}-\bar{f}_{3T})/\bar{F}_{3T}, \quad \text{etc.}$$

For the hcp lattice, $\bar{\Omega}$ and $\bar{f}_{4T}$ are the same as for fcc, to the number of significant figures given in Table III. $\bar{f}_{3T}$ is more negative for hcp than for fcc by about 0.02 for each α and β; this difference represents the additional term in (4.7) for the hcp lattice. The errors in the approximations $\bar{f}_{3T}$, $\bar{f}_{4T}$, and $\bar{f}_{3T}+\bar{f}_{4T}$ are essentially the same for hcp as for fcc.

An alternate approximation, namely, that of averaging the diagonal elements of $\lambda_{\mathbf{k}}$ instead of those of $\mathbf{a}_{\mathbf{k}}$, has also been investigated. This procedure is expressed by writing

$$\lambda_{\mathbf{k},\rho\rho'}=\theta\delta_{\rho\rho'},$$
$$\theta=(3JN)^{-1}\sum_{\mathbf{k}}\sum_{\rho}\lambda_{\mathbf{k},\rho\rho}. \tag{4.11}$$

This approximation is quite poor for both fcc and hcp. It leads to results for $\bar{f}_{4T}$ which are too large in magnitude by a factor of 3 to 4, and to results for $\bar{f}_{3T}$ which are too large in magnitude by a factor of 4 to 6. This result is in agreement with the similar conclusion of Leibfried and Ludwig.[12]

For purposes of comparison, the result obtained previously by a different approximation[5] has been transformed to the same units as those used in the present work. This result applies to a fcc lattice with nearest and next-nearest neighbors included, and to the case of $\alpha=12$, $\beta=6$ in the Lennard-Jones potential. The values of $\bar{f}_{3T}$ and $\bar{f}_{4T}$ are listed in Table III. These contributions are each less accurate than for the approximation defined by (4.1), but the sum $(\bar{f}_{3T}+\bar{f}_{4T})$ is more accurate. In order to extend this approximation to other potential functions, it would be necessary to repeat a large part of the calculation. This approximate calculation is considerably more complicated than is the evaluation of Eqs. (4.7)–(4.9).

Maradudin et al.[6] have carried out an approximate calculation for the fcc lattice for nearest neighbors only. These authors obtained a result for a two-body central potential of arbitrary form. This approximation, when translated into the language of the present paper, is

$$\bar{f}_{3T}=-N(KT)^2[0.01402\epsilon^2/\Phi^3]$$
$$\times[9(\phi'')^2+12\phi''\phi'''\epsilon^2+4(\phi''')^2\epsilon^4], \tag{4.12}$$

$$\bar{f}_{4T}=N(KT)^2[3/64\Phi^2][3\phi''+12\phi'''\epsilon^2+4\phi^{\text{iv}}\epsilon^4], \tag{4.13}$$

where

$$\Phi=\tfrac{1}{2}\phi'+\phi''\epsilon^2. \tag{4.14}$$

Here all derivatives of ϕ are evaluated at the nearest-neighbor distance. Although this approximation was derived with $\phi'=0$, which is appropriate for a nearest-neighbor model, ϕ' is retained here since it appears when the original expressions of Ref. 6 are transformed into the present notation. The contribution of the ϕ' term is quite small in all of the calculations presented here.

Equations (4.12)–(4.14) are quite similar in form to the approximation developed above, as represented by (4.7) and (4.8). This similarity is brought out more fully if the Ω of (4.7) and (4.8) is calculated for nearest neighbors only. The result is

$$\Omega=16[(3/2)\phi'+\phi''\epsilon^2)]; \quad \text{fcc, nearest neighbors.} \tag{4.15}$$

Equations (4.12) and (4.13) have been evaluated for the Lennard-Jones models and the results are listed in Table III. It is seen that this approximation is slightly less accurate, in general, than that represented by (4.7) and (4.8). For (4.12) and (4.13) $\delta(\bar{f}_{3T}+\bar{f}_{4T})$ is very close to twice that for the approximation of the present paper, for each case of α and β.

Leibfried and Ludwig have proposed two possible approximations for F_{3T} and F_{4T}.[12] In the case that all the atoms of the crystal have the same mass, their first approximation is identical to the one defined by (4.1). For such a case, Ω is the average of the eigenvalues of the $\mathbf{a}_{\mathbf{k}}$ matrices:

$$\Omega=(3JN)^{-1}\sum_{\mathbf{k}s}M(\omega_{\mathbf{k}s})^2, \quad \text{all} \quad M_j=M. \tag{4.16}$$

In addition, these authors have carried out numerical calculations for their second approximation for the fcc lattice for some Lennard-Jones models. In each case where they have used the same α and β as those in Table III, their results for $\bar{f}_{3T}$ and $\bar{f}_{4T}$ agree with the present approximation [Eqs. (4.7)–(4.9)] within 1%. Thus, the present approximation appears generally to be in quantitative agreement with those of Leibfried and Ludwig for the case where all masses are the same.

It is of interest to note that the approximations discussed in this section are of two qualitatively different types. The approximation defined by (4.1), and those of Refs. 5 and 12, are based upon an approximate representation of the functions of the normal-mode frequencies which occur in the expressions for F_3 and F_4. The result of Ref. 6 is based upon an approximate representation of the B and C coefficients which occur in the expressions for F_3 and F_4.

All of the data of Table III, with the exception of the values taken from Ref. 5, were obtained with the aid of a desk calculator in a few days.

V. DISCUSSION

Several qualitative conclusions can be drawn from the results of the accurate calculations of Sec. III. For the Lennard-Jones models, F_{3T} is always negative and is fairly insensitive to the range of forces, while F_{4T} is always positive and decreases markedly with increasing range of forces. $(F_{3T}+F_{4T})$ is positive for all the models chosen, and hence C_{VT} is negative, but these quantities become quite small as the range of forces increases. It is likely that these trends will hold for any central-force model, although from the present work it is not possible to say anything about the case of Coulomb forces. It also appears likely that, for any model based

on short-range forces, the anharmonic specific heat at constant volume will be negative at high temperatures for fcc and hcp lattices.

Indeed, there is a great similarity between the results for fcc and those for hcp. Although this similarity might well be expected, on the basis of the similarity of the two lattice structures, it is certainly not apparent in the general formulation of Sec. I. In the approximation of Sec. IV, however, as defined by (4.1) and expressed by (4.3) and (4.4), it appears that the fcc and hcp should give quantitatively similar results for any force model. For two-body central forces and nearest neighbors only, (4.7), (4.8) and (4.15) show that the approximation gives results for fcc and hcp which are identical, except for the $B_{0i,0i',0i''}$ terms. Note that, for nearest neighbors only, (4.15) is valid for the hcp lattice also.

In general, F_{3T} and F_{4T} do not depend explicitly on the masses of the ions; this is a consequence of the equipartition of energy at high temperatures. In addition, F_{3T} and F_{4T} do not depend explicitly upon the nearest-neighbor distance ϵ, but only implicitly through the dependence on ϵ of the potential functions. As pointed out above,[11] ϵ may depend upon the masses, thus bringing some mass dependence into F_{3T} and F_{4T}. The anharmonic contributions to the free energy should be fairly insensitive to the choice of ϵ; this point is being investigated further.

With respect to the numerical work, it is felt that the use of the inverse dynamical matrix offers the simplest method for an accurate calculation of the high-temperature anharmonic free-energy contributions. In addition, it is felt that a sum over the first Brillouin zone can be carried out directly, to a given accuracy, with much greater ease than by the more traditional method of transforming such a sum to an integral over normal mode frequencies. This applies to any sum over the zone, and if only a part of the zone is counted in the sum, the use of weighting factors is necessary. If the summand varies strongly within the first zone, such as an exponential function, the accuracy can be maintained by the use of an interpolation procedure such as Simpson's rule; such procedure was not required in the present calculations.

One of the greatest values of the accurate calculations is to enable the evaluation of approximations. From the comparison with the accurate results, it is concluded that the present approximation, as defined by (4.1), is perhaps the best one currently available in terms of simplicity and accuracy. In addition, the present approximation has the advantage of being formulated in general, and can readily be applied to any force model and any crystal structure. It is reasonable to expect that the present approximation will have qualitatively the same errors as those listed in Table III, for other crystal structures, and other force models with comparable ranges of forces. The approxi-

mations discussed in Sec. IV are most likely inadequate for the case of Coulomb forces.

To be sure, the accuracy of the approximations is not entirely satisfactory. The present approximation represents $\bar{F}_{4T}$ with good accuracy, for all cases calculated, while for $\bar{F}_{3T}$ the errors are larger and increase with increasing range of forces. This might be expected since, in general, the expressions for F_4 are much simpler than those for F_3. All the approximations give a result for $\bar{F}_{3T}$ which is correct in sign, but too small in magnitude. As a result, the error in an approximation to $(\bar{F}_{3T}+\bar{F}_{4T})$ is usually larger than the error in either contribution alone.

For the present approximation, the higher order terms in (1.13) and (1.14) reduce to expressions similar to those given by (4.3)–(4.8) for the various special cases. In fact, the only differences are in the denominators, where Ω becomes replaced by other simple functions. The approximation should be at least as accurate for these higher order terms as for the leading terms.

Finally, certain general limitations on the present calculations should be pointed out. Hooton[13] has shown that the perturbation treatment of the anharmonic free energy of crystals is generally valid for all except the lighest elements, hydrogen and helium. Within the framework of the perturbation treatment, the restriction to the lowest contributing orders is a good approximation as long as the anharmonic energy of each normal mode is small compared to the harmonic energy of that mode. In practice, this condition is probably satisfied, in the high-temperature limit, to a temperature several times greater than the Debye temperature, and perhaps to the melting temperature. The particular limitations imposed by the restriction to a Lennard-Jones model are being investigated.

ACKNOWLEDGMENTS

APPENDIX: TRANSFORMATION OF DYNAMICAL MATRIX TO REAL, SYMMETRIC FORM

For the case of two atoms per unit cell, the a_k matrices are in general complex. For numerical work, it is convenient to avoid complex arithmetic by transforming a_k to real, symmetric form. This can be accomplished

[13] D. J. Hooton, Phil. Mag. 46, 422, 433 (1955).

by the unitary transformation (independent of $\mathbf{k}$)[14]

$$\mathbf{t}=\frac{1}{\sqrt{2}}\begin{pmatrix}1 & i\\ i & 1\end{pmatrix}, \quad \text{for each } \mathbf{k}, \qquad (A1)$$

where the submatrices of $\mathbf{t}$ are multiples of the unit matrix of order 3. Then, suppressing the index $\mathbf{k}$, if κ of (2.12) is written as $\kappa_0+i\kappa_1$, where κ_0 and κ_1 are real and symmetric,

$$\mathbf{d}=\mathbf{t}^{-1}\mathbf{a}\mathbf{t}=\begin{pmatrix}\gamma-\kappa_1 & \kappa_0\\ \kappa_0 & \gamma+\kappa_1\end{pmatrix}. \qquad (A2)$$

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[14] This transformation has been used by L. J. Slutsky and C. W. Garland, J. Chem. Phys. **26**, 787 (1957).

$\mathbf{d}$ is easily inverted numerically to obtain $\mathbf{\mu}=\mathbf{d}^{-1}$. If $\mathbf{\mu}$ is represented in submatrix form as

$$\mathbf{\mu}=\begin{pmatrix}\mu_1 & \mu_2\\ \mu_3 & \mu_4\end{pmatrix}, \qquad (A3)$$

then $\lambda=\mathbf{t}\mathbf{\mu}\mathbf{t}^{-1}$ gives rise to the relations

$$\begin{aligned}\eta&=\tfrac{1}{2}[(\mu_1+\mu_4)+i(\mu_3-\mu_2)],\\ \zeta&=\tfrac{1}{2}[(\mu_2+\mu_3)+i(\mu_4-\mu_1)].\end{aligned} \qquad (A4)$$

These results are valid for any lattice with two atoms per unit cell for the case of central forces.

Variational Theory of Paramagnetic Impurities in Van der Waals Crystals*†

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A consistent method of calculating the wave functions and electron-spin-resonance properties of a dilute paramagnetic impurty in a molecular crystal is outlined, and the system of atomic hydrogen in solid argon is treated as a detailed example. Starting from a one-electron, tight-binding, static-lattice picture of the impurity-doped crystal, the crystal wave function is formed as the antisymmetrized product of atomic Hartree-Fock functions. This is modified for the interactions in the crystal by adding variational corrections for crystal field effects, the spin-orbit interaction, and the Van der Waals interaction. The spin-resonance parameters are then found from the expectation value of the interaction with a magnetic field. The results lead to a reintepretation of parameters in previous theories and show that the various crystal perturbations do not add independently to give a net result when there is appreciable overlap between the impurity and host atoms. Estimates of the electronic g factor for hydrogen in argon are in good agreement with experiment. The predicted hyperfine shifts for substitutional hydrogen impurities also agrees well. However, it is shown that for interstitial sites the hyperfine-shift calculations are unreliable.

I. INTRODUCTION

RECENTLY both spin-resonance and optical-absorption spectra of isolated impurities trapped in rare-gas solids have been observed.[1-4] The outstanding feature of the results is that the spectrum of a dilute impurity is changed only slightly from the free-state spectrum by the crystal environment. Several theoretical treatments relating these shifts to the polarizability, spin-orbit splitting, etc., of the impurity and the host lattice have been given for specific systems. In

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[1] C. K. Jen, S. N. Foner, E. L. Cochran, and V. A. Bowers, Phys. Rev. **104**, 846 (1956).

[2] S. N. Foner, E. L. Cochran, V. A. Bowers, and C. K. Jen, J. Chem. Phys. **32**, 963 (1960).

[3] J. P. Goldsborough and T. R. Koehler, Bull. Am. Phys. Soc. **7**, 449 (1962).

[4] M. McCarty and G. Robinson, Mol. Phys. **2**, 415 (1959).

these, additivity of the effects of the various crystal perturbations has been assumed and experimental data have been used to evaluate parameters in the models.[4,5]

The present work outlines a calculation of the ground-state wave function and electron-spin-resonance parameters of a tight-binding paramagnetic center in a rare-gas crystal. It is a "first principles" calculation in the sense that experimentally determined quantities are not used, and the major perturbations due to the crystal environment are calculated simultaneously so that effects depending on two or more interactions are retained. Specifically, the theory developed has been applied to the case of atomic hydrogen in argon, and order-of-magnitude estimates have been made as a guide for applying the theory in detail. Excited states and, therefore, optical properties could be treated, but more attention to overlap effects would be necessary.[6]

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[5] F. Adrian, J. Chem. Phys. **32**, 972 (1960).

[6] For a review see D. L. Dexter, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 6, p. 353. Examples of calculations include R. S. Knox, J. Phys. Chem. Solids **9**, 265 (1959); A. Gold, *ibid.* **18**, 218 (1961); Phys. Rev. **124**, 1740 (1961).