# THE THERMODYNAMIC QUANTITIES OF A PERFECT CRYSTAL LATTICE IN THE HARMONIC APPROXIMATION

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It is shown that the distribution function for the squares of the frequencies of an ideal lattice is represented in the form of the arithmetic mean of the spectral densities of several Hermitian operators with simple spectra. On the basis of this representation, a method is advanced for the approximation of the mean values with respect to the lattice spectrum. The approximation of the thermodynamic means is expressed as the sum of analytic functions. A knowledge of the force constants matrix is sufficient for determining the quadrature formulas. The method is illustrated by the calculation of the thermodynamic characteristics of a model of a face-centered lattice involving interaction between nearest neighbors. Quadrature formulas are presented for this case. The calculated temperature dependence of the specific heat is compared with the experimental values for solid xenon. The agreement of theory with the experimental data over a broad temperature range (T $\lesssim$ 60°K) lies within the experimental errors.

## 1. INTRODUCTION

$\mathbf{T}$HE calculation of the thermodynamic characteristics of a crystal lattice in the harmonic approximation reduces to finding the vibration spectrum of the crystal.

As is well known (see, for example, [1]), any thermodynamic function $F(T)$ of a crystal lattice is represented in the form

$$F(T) = 3rN \int f(\lambda, T) g(\lambda) d\lambda, \qquad (1)$$

where r is the number of atoms in the unit cell of the lattice; N is the number of unit cells in the crystal, $f(\lambda, T)$ is some function of the frequency of natural oscillations of the crystal, of the absolute temperature T and, possibly, of other parameters; $g(\lambda)$ is a function defining the relative number of vibrational states of the lattice, the squares of the frequencies of which $\lambda$ lie in the interval $(\lambda, \lambda + d\lambda)$. The form of the function $f(\lambda, T)$ is determined by the desired thermodynamic quantity $F(T)$. The function $g(\lambda)$ satisfies the normalization condition

$$\int g(\lambda) d\lambda = 1. \qquad (2)$$

The Debye approximation function for $g(\lambda)$ is usually employed in calculations of quantities of the type (1). As is well known, this approximation gives a satisfactory description of the lattice properties only in the region of extremely low temperatures.

When one starts out from a specific microscopic model of the crystalline lattice in the same cases, however, the calculation of the function $g(\lambda)$ entails great difficulties, and reduces in the end to finding $g(\lambda)$ in the form of a plot or a table. This circumstance leads to the necessity of the development of an approximation of the mean values over the spectrum of the lattice. Perhaps the only effective method of approximation of integrals of the form (1) is the method of Thirring,[2] which is based on expansion of $f(\lambda, T)$ under the integral in a power series in $\lambda$ and on the subsequent calculation of the moments $\int \lambda^n g(\lambda) d\lambda$ of the distribution function $f(\lambda)$. However, by virtue of the specific nature of the functions $f(\lambda, T)$ of interest, the region of applicability of

this method is exhausted by the region of comparatively high temperatures (T > $2\Theta/3\pi$, where $\Theta$ is the characteristic temperature).

In the present paper, a new method is proposed for approximating integrals of the form (1) with any desired algebraic accuracy[3] over the entire region of change of the temperature T. The method is based on the approximation of the function $g(\lambda)$ by functions of the form

$$g_n(\lambda) = \sum_{i=1}^{n} \mu_i^{(n)} \delta(\lambda - \lambda_i^{(n)}), \qquad (3)$$

where the numbers $\mu_i^{(n)}$ and $\lambda_i^{(n)}$ are determined by the equations of motion of the lattice, while the number of components in (3) follows from the required accuracy of the approximation.

If $F_n(T) = \int f(\lambda, T) g_n(\lambda) d\lambda$, then the absolute error $|F(T) - F_n(T)|$ is seen in practice to be much less than the theoretical estimate of this error, which is equal to twice the maximum deviation from the function $f(\lambda, T)$ of the best-approximation polynomial of degree $2n - 1$. It then follows that the absolute error of the calculation of such quantities as the specific heat of the lattice falls off exponentially with the number n. The approximation of the spectral density $g(\lambda)$ by sums of the form (3) is based on a theorem proved in the paper, which asserts that the function $g(\lambda)$ of an ideal crystal lattice is represented in the form of the arithmetic mean of the spectral densities of several Hermitian operators with simple spectra.[1)]

As an illustration of the application of the method, results are given of the calculation of thermodynamic functions for the case of a face-centered cubic lattice with central interaction of nearest neighbors (elastic coupling). The computed temperature dependence of the specific heat at constant volume is compared with the experimental data for crystalline xenon. Excellent

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[1)]In order that there be no derivation from the terminology used in the mathematical literature cited below, the term "simple spectrum" is used everywhere in the paper in place of the term "non-degenerate spectrum" commonly used in physics.

agreement is found here over a wide temperature range.

With some alterations, the idea of the method presented in this paper can be used effectively for the calculation of the change brought about in thermodynamic functions by local lattice defects. The method makes it possible to find some special types of monochromatic vibrations of the lattice that are of interest in their own right. The proposed method can also be used for the investigation of the stability of crystal lattices.

## 2. APPROXIMATION OF THE MEAN VALUES OVER THE VIBRATION SPECTRUM

The set of equations describing the harmonic vibrations of a crystal lattice has the form

$$m_R \ddot{u}_R^\sigma = - \sum_{R'\sigma'} A_{RR'}^{\sigma\sigma'} u_{R'}^{\sigma'}, \tag{4}$$

where $u_R^\sigma$ is the $\sigma$th component in some rectangular system of coordinates of the displacement vector $u_R$ of an atom vibrating about the equilibrium position $R$; $m_R$ is the mass of this atom; the tensor $A_{RR'}$ describes the interaction between the lattice atoms, and the summation is carried out over all $R'$ and $\sigma'$. After the transformation $u_R = (m_R)^{-1/2} e^{i\omega t} \chi(R)$, the set of equations (4) is rewritten in the form

$$\sum_{\sigma', R'} L_{RR'}^{\sigma\sigma'} \chi^{\sigma'}(R') = \lambda \chi^\sigma(R), \tag{5}$$

where $\lambda = \omega^2$ and $L_{RR'}^{\sigma\sigma} = (m_R m_{R'})^{-1/2} A_{RR'}$ are the matrix elements of a certain Hermitian operator $L$. The matrix of the operator $L$ in the given representation is usually called the force-constants matrix. It is convenient to rewrite the set of equations (5) in the form of a single equation

$$L\chi = \lambda\chi, \tag{6}$$

where $\chi$ is a multidimensional vector whose components in some basis are enumerated by the indices $R$ and $\sigma$. Solution of the set of equations (4) is equivalent to finding the eigenvalues and eigenfunctions of the operator $L$. The eigenvalues of the operator $L$ give us the squares of the natural frequencies of the system, while the eigenvectors $\chi$ determine the amplitudes of the vibrations of the atoms of the lattice.

We denote by $H$ the space in which the action of the operator $L$ is defined. In this space, we choose an arbitrary orthonormal basis $a_1, a_2, \ldots, a_{3rN}$. As is well known, the mean value of the arbitrary function $f(\lambda, T)$ over the spectrum of the operator $L$, together with the representation (1), can be written in the form

$$F(T) = Sp\{f(L, T)\} = \sum_{i=1}^{3rN} [a_i, f(L, T) a_i], \tag{7}$$

where the scalar product in the space $H$ is denoted by means of the square brackets. If the basis $a_1, a_2, \ldots, a_{3rN}$ is so chosen that the first $3r$ vectors $a_1, a_2, \ldots, a_{3r}$ also form a basis in the space of displacements of the atoms belonging to a single elementary cell, then Eq. (7) is greatly simplified by virtue of the periodicity of the lattice and of the cyclic conditions of Born and von Karman, taking the form

$$F(T) = N \sum_{i=1}^{3r} [a_i, f(L, T) a_i]. \tag{8}$$

Thus the calculation of thermodynamic functions reduces to the calculation of $3r$ matrix elements $[a_i, f(L, T) a_i]$ of the operator $f(L, T)$ ($i = 1, 2, \ldots, 3r$), where $r$ is the number of atoms in the unit cell.

It is not difficult to establish the fact that the effect of the operator $f(L, T)$ on the arbitrary vector $a_i$ of the space $H$ translates this vector, regardless of the form of the function $f(\lambda, T)$, into the subspace $H_i$, spanned by the vectors

$$a_i, \quad La_i, \quad L^2 a_i, \ldots \tag{9}$$

This subspace is invariant relative to the operator $L$. Therefore the operator $L$ induces some operator $L_i$ in the subspace $H$. Consequently, the matrix elements of the operator $f(L, T)$ are seen to be equal to the matrix elements $[a_i, f(L_i, T) a_i]$, i.e.,

$$[a_i, f(L, T) a_i] = [a_i, f(L_i, T) a_i]. \tag{10}$$

As is known from the theory of linear operators (see, for example, [4,5]),

$$[a_i, f(L_i, T) a_i] = \int f(\lambda, T) g_i(\lambda) d\lambda, \tag{11}$$

$$g_i(\lambda) = \frac{d}{d\lambda} [a_i, E_\lambda^{(i)} a_i],$$

where $E_\lambda^{(i)}$ is the orthogonal spectral function[2] of the operator $L_i$.

It follows from (1), (8) and (11) that

$$g(\lambda) = \frac{1}{3r} \sum_{i=1}^{3r} g_i(\lambda). \tag{12}$$

It is easy to show (see, for example, [4]) that the operators $L_i$ are Hermitian operators with simple spectra. Therefore Eq. (12) is equivalent to the statement that the function $g(\lambda)$ of the distribution of squares of the distribution of squares of the frequencies of an ideal lattice is represented in the form of the arithmetic mean of the spectral densities $g_i(\lambda)$ of several Hermitian operators with simple spectra.

It also follows from Eq. (12) that knowledge of the functions $g_i(\lambda)$ suffices for averaging over the spectrum of an ideal lattice. The exact calculations of the functions $g_i(\lambda)$ is obviously impossible in the general case. However, the fact that the functions $g_i(\lambda)$ are the spectral densities of the Hermitian operators $L_i$ with simple spectra makes it possible, as is shown below, to demonstrate the effective approximation of the functions $g_i(\lambda)$, which makes it possible to compute integrals of the form $\int f(\lambda) g_i(\lambda) d\lambda$ with great accuracy.

If we choose the normalized vectors $g_0^{(i)} = a_i, g_1^{(i)}, g_2^{(i)}, \ldots$ (which are obtained by the successive orthogonalization of the vectors $a_i, La_i, L^2 a_i, \ldots$) as the bases in the subspace $H_i$, then the matrices of the operators $L_i$ in these bases are represented by the Jacobi matrices

$$L_i = \begin{pmatrix} (L_i)_{00} & (L_i)_{01} & 0 & 0 & \cdots \\ (L_i)_{10} & (L_i)_{11} & (L_i)_{12} & 0 & \cdots \\ 0 & (L_i)_{21} & (L_i)_{22} & (L_i)_{23} & \cdots \\ 0 & 0 & (L_i)_{32} & (L_i)_{33} & \cdots \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots \end{pmatrix}. \tag{13}$$

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[2] The orthogonal spectrum function $E_\lambda$ of the operator $L$ is defined as the projection operator on the subspace generated by all the eigenfunctions of the operator $L$, which belong to eigenvalues less than $\lambda$.

Let us find the eigenfunctions $\chi_\lambda^{(i)}$ of the operators $L_i$ in the subspace $H_i$.[3] We seek these eigenfunctions in the basis $g_0^{(i)}$, $g_1^{(i)}$, $g_2^{(i)}$, ..., i.e., in the form

$$\chi_\lambda^{(i)} = A_i(\lambda) \sum_{n=0}^{\infty} P_n^{(i)}(\lambda) g_n^{(i)}, \qquad (14)$$

where $A_i(\lambda)$ is the normalized coefficient and $P_0^{(i)}(\lambda) = 1$. Substituting (14) in the equation $(L_i - \lambda)\chi_\lambda^{(i)} = 0$, in accord with (13), we get the following set of recurrence relations for the coefficients $P_n^{(i)}(\lambda)$:

$$(L_i)_{n,n-1} P_{n-1}^{(i)}(\lambda) + (L_i)_{n,n} P_n^{(i)}(\lambda) + (L_i)_{n,n+1} P_{n+1}^{(i)}(\lambda) = \lambda P_n^{(i)}(\lambda). \quad (15)$$

This set of recurrence relations makes it possible to calculate the quantities $P_n^{(i)}(\lambda)$ systematically. By virtue of the fact that $P_0^{(i)}(\lambda) = 1$, it follows from (15) that $P_n^{(i)}(\lambda)$ is a polynomial of degree n. If we choose the function $\chi_\lambda^{(i)}$ to be normalized by the condition $|\chi_\lambda^{(i)}, \chi_{\lambda'}^{(i)}| = \delta(\lambda - \lambda')$, where $\delta(\lambda - \lambda')$ is the Dirac delta function, then it follows from the completeness of the set of functions $\chi_\lambda^{(i)}$ in the subspace $H_i$ that the polynomial $P_n^{(i)}(\lambda)$ should satisfy the following orthogonality condition:

$$\int P_m^{(i)}(\lambda) P_n^{(i)}(\lambda) A_i^2(\lambda)\, d\lambda = \delta_{mn}. \qquad (16)$$

The equality

$$[a_i, f(L_i, T) a_i] \equiv [g_0^{(i)}, f(L, T) g_0^{(i)}] = \int f(\lambda, T) A_i^2(\lambda)\, d\lambda \qquad (17)$$

also follows from the orthogonality condition (16). To prove (17) it suffices to express $g_0^{(i)}$ in the form of an expansion in the functions $\chi_\lambda^{(i)}$:

$$g_0^{(i)} = \int [\chi_\lambda^{(i)}, g_0^{(i)}] \chi_\lambda^{(i)}\, d\lambda.$$

Comparing (11) and (17), we establish the result that

$$g_i(\lambda) = A_i^2(\lambda). \qquad (18)$$

Thus the polynomials $P_n^{(i)}(\lambda)$ are orthogonal relative to the weight $g_i(\lambda)$. As is known,[3] it suffices to know two neighboring polynomials $P_{n-1}^{(i)}(\lambda)$ and $P_n^{(i)}(\lambda)$, orthogonal with weight $g_i(\lambda)$, to be able to obtain some information on the behavior of the integrals (11). Actually, knowledge of the polynomials $P_{n-1}^{(i)}(\lambda)$ and $P_n^{(i)}(\lambda)$ makes it possible to construct the quadrature formula

$$\int f(\lambda) g_i(\lambda)\, d\lambda = \sum_{h=1}^{n} \mu_h^{(i,n)} f(\lambda_h^{(i,n)}) \qquad (19)$$

for the integral (11), where $\lambda_k^{(i,\,n)}$ are the roots of the equation $P_n^{(i)}(\lambda) = 0$, while the numbers $\mu_k^{(i,\,n)}$ are found from the relation[4]

$$\mu_k^{(i,n)} = \left\{ (L_i)_{n-1,n} P_{n-1}^{(i)}(\lambda) \frac{d}{d\lambda} P_n^{(i)}(\lambda) \right\}^{-1} \Bigg|_{\lambda = \lambda_k^{(i,n)}}. \qquad (20)$$

Equation (19) is the quadrature formula of highest algebraic accuracy. This means that Eq. (19) is accu-

rate if $f(\lambda)$ is an arbitrary polynomial of degree not exceeding $2n - 1$. Therefore, the approximation of the integrals $\int f(\lambda) g_i(\lambda) d\lambda$ for any function $f(\lambda)$ gives an error less than twice the maximum deviation of the polynomial of the best approximation (of degree $2n - 1$) of the function $f(\lambda)$ over the spectrum of the operator $L_i$. Since the spectrum of the operator $L_i$ is bounded, one can achieve great accuracy for the value of the integral (11) with only a small number of components in Eq. (19). It is evident that the convergence of the approximation (19) with increasing n is very rapid.

Thus it follows from (12) and (19) that, in the calculation of thermodynamic functions, the function $g(\lambda)$ of the distribution of squares of frequencies of the lattice can be approximated by expressions of the form

$$g(\lambda) = \frac{1}{3r} \sum_{i=1}^{3r} \sum_{h=1}^{n_i} \mu_k^{(i,n_i)} \delta(\lambda - \lambda_k^{(i,n_i)}). \qquad (21)$$

This approximation gives the probability of finding the values of integrals of type (1) with great accuracy. Calculations of thermodynamic functions by means of the quadrature formulas (19) show that this approximation, even with only a small number of components in (19), gives entirely satisfactory accuracy in the region of medium and high temperatures. In the next section we give, by way of illustration, the results of calculation of some thermodynamic mean values for the case of a model of a face-centered lattice with central interaction of the nearest neighbors.

## 3. ILLUSTRATIONS OF THE METHOD

As an example, let us consider a single-atom face-centered cubic lattice with nearest-neighbor interaction.

As the vectors of displacement of an atom lying in a fundamental unit cell, it is convenient to choose unit displacements along fourfold axes. Because of the symmetry of the lattice, the distribution function $g(\lambda)$ of the squares of the frequencies for the cubic single-atom lattice, according to (12), is identical with $g_i(\lambda)$, where $g_i(\lambda)$ is the spectral function induced by the displacement of the atom along one of the fourfold axes. We denote the unit displacement of the atom along this axis by $\mathbf{a}$. The direction of the vector $\mathbf{a}$ in symmetry transformations which keep the origin of the coordinates fixed is transformed into another equivalent direction along one of the series of irreducible representations $\Gamma_5^-$ (in the notation of Bethe[6]) of the point group $O_h$. Consequently, the subspace $\mathbf{a}$, $L\mathbf{a}$, $L^2\mathbf{a}$, ... is also transformed along this same series of irreducible representation $\Gamma_5^-$. Therefore, for convenience of calculation, it is useful to choose in each coordination sphere a basis which is transformed similarly to the vector $\mathbf{a}$. Inasmuch as we shall not be interested in the eigenfunctions of the operator $L$ in the subspace $\mathbf{a}$, $L\mathbf{a}$, $L^2\mathbf{a}$, ... in the present work, we shall write down the final form of the matrix (13) for the model of the lattice selected by us, without going into the details of the calculation.

For simplicity, we take the matrix $L$ in the following form:

$$(L_{000}^{ik}) = \frac{\lambda_m}{2} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad (L_{011}^{ik}) = -\frac{\lambda_m}{16} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 1 \\ 0 & 1 & 1 \end{pmatrix}, \qquad (22)$$

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[3] The eigenfunctions $\chi$ of the operators $L_i$ are of intrinsic interest in many problems on the vibrations of the lattice. This problem is not discussed in this paper.

[4] To write down the formula (20) (see [3], Eq. (7.14)), we have taken it into account that the ratio of the coefficients for the leading powers of the polynomials $P_{n-1}^{(i)}(\lambda)$ and $P_n^{(i)}(\lambda)$ is equal to $(L_i)_{n-1,n}$. This follows directly from (15).

where $\lambda_m$ is the maximum eigenvalue of the operator L. The remaining matrices of the operator L are obtained from (22) by application of the symmetry operations of the group $O_h$ (see [7]). The following values are obtained for the matrix elements of the matrix (13):

$$L_{00} = 0{,}5\lambda_m, \quad L_{11} = 0{,}5625\lambda_m, \quad L_{22} = 0{,}45089\lambda_m,$$
$$L_{33} = 0{,}50753\,\lambda_m, \quad L_{44} = 0{,}51289\,\lambda_m, \ldots;$$

$$L_{10} = L_{01} = -0{,}25\,\lambda_m, \quad L_{12} = L_{21} = -0{,}23385\,\lambda_m,$$
$$L_{23} = L_{32} = -0{,}24227\,\lambda_m, \quad L_{34} = L_{43} = -0{,}26053\,\lambda_m, \ldots \quad (23)$$

These values of the matrix elements make it possible for us to find the first few polynomials $P_n(\lambda)$ ($n \leq 5$). By finding the roots of these polynomials and, by means of Eq. (20), the terms $\mu_k^{(n)}$, we can write down the sequence of quadrature formulas (19) with different values of n (n = 1, 2, 3, 4, 5) for the integrals $F = \int f(\lambda)g(\lambda)\,d\lambda$:[5]

$$n = 1, \quad F = f(0{,}5\lambda_m); \quad (24)$$
$$n = 2, \quad F = 0{,}5620 f(0{,}2793\lambda_m) + 0{,}4380 f(0{,}7832\lambda_m); \quad (25)$$
$$n = 3, \quad F = 0{,}2554 f(0{,}1737\lambda_m) + 0{,}4826 f(0{,}4743\lambda_m)$$
$$+ 0{,}2620 f(0{,}8654\lambda_m); \quad (26)$$
$$n = 4, \quad F = 0{,}1187 f(0{,}1127\lambda_m) + 0{,}4402 f(0{,}3495\lambda_m)$$
$$+ 0{,}2662 f(0{,}6581\lambda_m) + 0{,}1750 f(0{,}9006\lambda_m); \quad (27)$$
$$n = 5, \quad F = 0{,}0617 f(0{,}0764\lambda_m) + 0{,}3038 f(0{,}2663\lambda_m)$$
$$+ 0{,}3237 f(0{,}4863\lambda_m) + 0{,}2079 f(0{,}7767\lambda_m)$$
$$+ 0{,}1029 f(0{,}9281\lambda_m). \quad (28)$$

We shall use the resultant quadrature formulas for the calculation of the energy $E_0$ of the zero-point vibrations of a crystal lattice. As is well known, the energy of the zero-point vibrations of a crystal lattice, taken for a single atom, is expressed by the formula

$$E_0 = {}^3/_2 \hbar \int \sqrt{\lambda}\, g(\lambda)\,d\lambda, \quad (29)$$

where $\hbar$ is Planck's constant divided by $2\pi$. Using Eqs. (24)–(28), we get for the approximate value of the integral (29)

$$E_0^{(1)} = 1{,}060 \hbar \sqrt{\lambda_m}, \quad E_0^{(2)} = 1{,}027 \hbar \sqrt{\lambda_m}, \quad E_0^{(3)} = 1{,}024 \hbar \sqrt{\lambda_m},$$
$$E_0^{(4)} = 1{,}023 \hbar \sqrt{\lambda_m}, \quad E_0^{(5)} = 1{,}0228 \hbar \sqrt{\lambda_m}. \quad (30)$$

It follows from the given values for $E_0$ that even the first approximation gives an error amounting at most to 3% of the calculated value, the second approximation giving an error of about 0.4%, the third, 0.1%, and the fourth, 0.02%, if the error is estimated relative to $E_0^{(5)}$. For an estimate of the error of the value of $E_0$ that has been found, we can compare the resultant values with the value

$$E_0 = (1{,}02266215 \pm 5 \cdot 10^{-9}) \hbar \sqrt{\lambda_m},$$

which was found by Isenberg.[8] As we see, in spite of the root singularity of the averaged function, even the second approximation gives a practically exact value for $E_0$.

As a second example, we calculate the specific heat of the crystalline lattice at constant volume for the model under consideration. As is well known, the specific heat at constant volume, referred to a single atom of the lattice, is given by the formula

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[5] A large number of figures after the decimal point are kept in Eqs. (25)–(28) in order that the rapid convergence of the sequence of quadratures (25)–(28) can be seen in the examples given below.

$$c_v = 3k \int \left(\frac{\hbar\sqrt{\lambda}}{2kT}\right)^2 \mathrm{sh}^{-2}\left(\frac{\hbar\sqrt{\lambda}}{2kT}\right) g(\lambda)\,d\lambda. \quad (31)$$

Here k is Boltzmann's constant.

Table I gives the results of the calculation of the integral (31) by the formulas (24)–(28) for different values of the ratio $T/\Theta$, where $\Theta = \hbar\sqrt{\lambda_m}/k$ is the characteristic temperature of the lattice. It is seen from the table that even the first approximation gives correct values of the specific heat (with an error not exceeding 0.5%) at temperatures $T \gtrsim \Theta/2$; the second approximation assures the same accuracy for a temperature $T \gtrsim \Theta/5$, the third for $T \gtrsim \Theta/7$, and the fourth for $T \gtrsim \Theta/10$. Since the specific heat approaches zero at low temperatures, the relative error at low temperatures increases rapidly. Therefore, the lower the temperature, the larger will be the number of terms necessary to include in the quadrature formula (19) in the calculation of the specific heat.

The results that have been given illustrate the effectiveness of the proposed method of calculation of the thermodynamic characteristics of the crystal lattice. The calculation of other thermodynamic quantities — the free energy, entropy, internal energy — confirms the rapid convergence of the quadrature formulas (19). In our opinion, one of the advantages of the proposed method is that the thermodynamic functions in such an approximation are represented as a sum of analytic functions.

In the near future, we shall show that the method described above is applicable to the calculation of the microscopic characteristics of a crystal lattice (both ideal and non-ideal), such as the average of the square of the displacement of an atom from its rest position, and the correlation of atoms in thermal motion. The calculation of such a quantity requires taking in the eigenfunctions (14) of the operator L.

## 4. COMPARISON WITH EXPERIMENT

It is of interest to compare the results obtained in the previous section with experiment.

Inasmuch as the model we have chosen takes into account only the interaction of nearest neighbors, the objects of such a comparison must obviously be molecular crystals, in particular, solid inert gases. In the present paper, we shall give a comparison of the computed temperature dependence of the specific heat $c_v$ theor at constant volume with the temperature dependence of $c_{v\,\mathrm{exp}}$ for xenon in the crystalline state.

The values of $c_{v\,\mathrm{exp}}$ were computed by use of the published data on the specific heat at constant pres-

**Table I**

| $T/\Theta$ | $c_v/3k$, computed from (24)–(28) | | | | |
|---|---|---|---|---|---|
|  | $n=1$ | $n=2$ | $n=3$ | $n=4$ | $n=5$ |
| 0,895 | 0,9496 | 0,9499 | 0,9499 | 0,9499 | 0,9499 |
| 0,8 | 0,9374 | 0,9379 | 0,9379 | 0,9379 | 0,9379 |
| 0,7 | 0,919 | 0,9201 | 0,9201 | 0,9201 | 0,9201 |
| 0,6 | 0,892 | 0,8936 | 0,8936 | 0,8936 | 0,8936 |
| 0,5 | 0,849 | 0,8520 | 0,8520 | 0,8520 | 0,8520 |
| 0,4 | 0,776 | 0,7827 | 0,7827 | 0,7827 | 0,7827 |
| 0,35 | 0,72 | 0,7302 | 0,7302 | 0,7302 | 0,7302 |
| 0,3 | 0,64 | 0,6589 | 0,6590 | 0,6590 | 0,6590 |
| 0,25 | 0,53 | 0,5612 | 0,5616 | 0,5616 | 0,5616 |
| 0,2 | 0,39 | 0,4290 | 0,4303 | 0,4304 | 0,4304 |
| 0,15 | 0,20 | 0,260 | 0,2650 | 0,2653 | 0,2653 |
| 0,1 | 0,04 | 0,035 | 0,096 | 0,0983 | 0,0986 |
| 0,05 | — | — | 0,004 | 0,007 | 0,0087 |

**Table II**

| $T/\Theta$ | $T^{\circ}$, K | $\dfrac{c_v \text{ theor}}{3k}$ | $\dfrac{c_v \text{ exp}}{3k}$ | $\dfrac{c_v\text{theor}-c_v \text{ exp}}{c_v\text{теор}}$, % |
|------|------|------|------|------|
| 0.895 | 54.4 | 0.950 | 0.943 | +0.7 |
| 0.8 | 48.6 | 0.938 | 0.938 | 0 |
| 0.7 | 42.6 | 0.920 | 0.923 | −0.3 |
| 0.6 | 36.5 | 0.894 | 0.897 | −0.3 |
| 0.5 | 30.4 | 0.852 | 0.852 | 0 |
| 0.4 | 24.3 | 0.783 | 0.777 | +0.7 |
| 0.35 | 21.3 | 0.730 | 0.724 | +0.8 |
| 0.3 | 18.25 | 0.659 | 0.659 | 0 |
| 0.25 | 15.2 | 0.562 | 0.569 | −1.3 |
| 0.2 | 12.16 | 0.430 | 0.433 | −0.7 |
| 0.15 | 9.12 | 0.265 | 0.263 | +0.8 |
| 0.1 | 6.08 | 0.0986 | 0.0973 | +1.3 |
| 0.0822 | 5.0 | 0.0542 | 0.0543 | −0.2 |
| 0.0658 | 4.0 | 0.0257 | 0.0254 | +1.2 |
| 0.0493 | 3.0 | $0.958 \cdot 10^{-2}$ | $0.956 \cdot 10^{-2}$ | +0.2 |
| 0.045 | 2.74 | $0.704 \cdot 10^{-2}$ | $0.700 \cdot 10^{-2}$ | +0.5 |
| 0.04 | 2.435 | $0.477 \cdot 10^{-2}$ | $0.477 \cdot 10^{-2}$ | 0 |
| 0.035 | 2.13 | $0.308 \cdot 10^{-2}$ | $0.312 \cdot 10^{-2}$ | −1.3 |

considered accidental. It then follows that the lattice model for which the calculations were carried out can describe the properties of xenon satisfactorily.

The model chosen in Sec. 3 corresponds to vibrations of the atoms of a face-centered, single-atom lattice about their static equilibrium positions for an arbitrary central interaction of nearest neighbors.

In conclusion, I express my gratitude to V. G. Manzheliĭ for his interest in the work.

sure,[9, 10] the density and the thermal expansion[11] and the isothermal compressibility.[12] As a reference point, which makes it possible to determine the value of the characteristic temperature $\Theta = \hbar\sqrt{\lambda_m}/k$, the specific heat $c_{v \text{ exp}}/3k = 0.659$ at $T = 18.25^{\circ}$K was chosen quite arbitrarily. A value of $\Theta$ of $60.8^{\circ}$K was then obtained. The results of the comparison are shown in Table II.

Theoretical values of the specific heat for the temperature range $0.1 \le T/\Theta < 0.895$ were obtained by means of the quadrature formula (28); the values of the specific heat for $T/\Theta < 0.1$ were computed from a quadrature formula of the type of formulas (24)−(28) with 11 components. (This formula is not given in the present paper.)

As is seen from the table, there is a remarkably good agreement between the calculated and experimental values. Taking it into account that the accuracy of the experiments,[9-12] the data of which were used for establishing Table II, is about 1%, we can conclude that the divergence of the theoretical and experimental lies within the limits of experimental error. The agreement with experiment is so good that it cannot possibly be

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