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Numerical Methods for Evaluating Integrals over First Brillouin Zones of Cubic Lattices*

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A new method is developed for evaluating the integral over the first Brillouin Zone of a face-centered cubic lattice. In this method the density of the points at which the value of the integrand is sampled increases towards the center of the zone, which makes the method particularly useful for the prediction of low-temperature thermodynamic properties. We use the new method and two other integration methods to evaluate the Debye specific heat formula, and compare the results to determine the relative usefulness of the different methods. We also discuss the application of the new method to the first Brillouin zone of the simple cubic lattice.

1. INTRODUCTION

Theoretical expressions for many of the observable properties of crystals involve one or more integrals of some function of the wave vector **k** over the region of reciprocal space known as the first Brillouin Zone (BZ). Such integrals are often obtained by considering a sample crystal of volume V and taking the limit $V \to \infty$ to obtain results that are independent of the sample size. For finite V, one obtains a sum over a uniformly distributed set of points, which in the limit $V \to \infty$ transforms to an integral according to the prescription

$$(8\pi^3/V)\sum_{\mathbf{k}} \to \int_{\mathrm{BZ}} d^3k. \tag{1}$$

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The integrals in the theoretical expressions for such thermodynamic properties as the specific heat C_V and the macroscopic Gruneisen function $\gamma(T)$ have integrands that at temperatures well below the Debye temperature are essentially zero except near the center of the BZ and that at temperatures well above the Debye temperature are of roughly the same order of magnitude everywhere within the BZ. Consequently, for an integration formula to be efficient at both low and high temperatures, the density of the points at which the integrand is sampled must increase towards the zone center, so that the integrand is sampled at a sufficient number of points to give accurate results at low temperatures without increasing the total sampling beyond what is necessary to give accurate results at high temperatures. An integration formula with a density of sampling points that increases towards the zone center can, of course, be helpful in the study of other than just thermodynamic properties.

Three different methods for obtaining integration formulas are considered. In Section 2 we review the commonly used *uniform mesh method* (UMM), which was described by Kellermann [1] in his classic paper on sodium chloride. This method samples the value of the integrand at a uniformly distributed set of points in the irreducible 1/48-th of the BZ. In Section 3 we introduce a new method, the *concentric region method* (CRM), which is an extension of the UMM. In the CRM the BZ is divided into a number of distinct concentric regions, each of which has the shape of a scaled-down BZ. The sampling density is kept uniform within each region but is changed from region to region to produce the desired increase in the sampling density towards the zone center. Finally, in Section 4 we discuss a *Gaussian method* (GM), which was introduced by Boyer and Hardy [2] to facilitate the calculation of the strain field around a point defect. This method also has a sampling density that increases towards the zone center. All three of these methods are designed for integrating smooth functions of $\mathbf{k}$, such as those that occur in the calculation of thermodynamic properties. They are not well suited for integrating functions that possess discontinuities or singularities at points other than at $\mathbf{k} = 0$. In particular, they are not well suited for evaluating the integral of the Dirac delta function $\delta(\omega - \omega_{\mathbf{k}})$, which yields the density of states function $g(\omega)$.

Specifically, we are concerned here with the evaluation of integrals of the form

$$\langle F \rangle \equiv (v_c/8\pi^3) \int_{\mathrm{BZ}} d^3k\, F(\mathbf{k}). \tag{2}$$

We are primarily interested in the case where the integration is over the BZ of the face-centered cubic (fcc) lattice, which is diagrammed in Fig. 1. We do, however, briefly consider the case where the integration is over the BZ of the simple cubic (sc) lattice in Section 3. The normalization factor $(v_c/8\pi^3)$ in Eq. (2) is such that, if $F(\mathbf{k}) = C$ for all $\mathbf{k}$, then $\langle F \rangle = C$. Here, v_c is the volume of the primitive cell of the lattice. For the fcc lattice $v_c = (a^3/4)$, where a is the lattice constant. For the

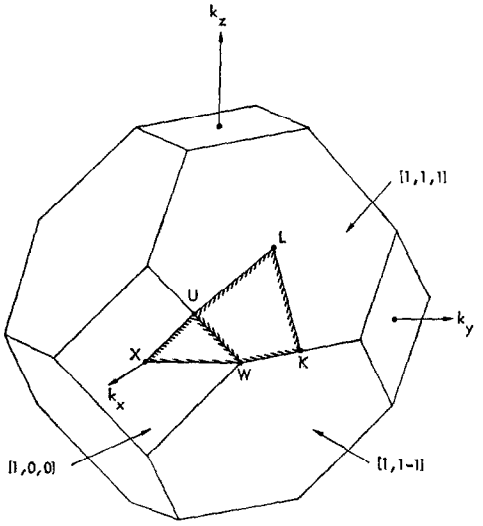

FIG. 1. The first Brillouin zone of the fcc lattice. The shaded part is the irreducible 1/48 of the zone. The numbers in square brackets give the direction of the normal to the surface indicated.

NaCl structure, $a = 2r$, where r is the distance between nearest neighbors. Since we are concerned with cubic lattices, we consider only integrands $F(\mathbf{k})$ that possess the cubic symmetry properties

$$\begin{aligned} F(k_x, k_y, k_z) &= F(k_y, k_x, k_z) = F(k_x, k_z, k_y) \\ &= F(-k_x, k_y, k_z) = F(k_x, -k_y, k_z) = F(k_x, k_y, -k_z) \end{aligned} \tag{3}$$

and the periodicity

$$F(\mathbf{k} + \mathbf{G}) = F(\mathbf{k}), \tag{4}$$

where $\mathbf{k} = (k_x, k_y, k_z)$, and $\mathbf{G}$ is any reciprocal lattice vector. Because of Eq. (3), the integral in Eq. (2) is equal to 48 times the integral over the irreducible 1/48-th of the BZ.

It is convenient to introduce the dimensionless variable $\mathbf{q}$ defined by

$$\mathbf{q} \equiv (a/2\pi)\,\mathbf{k}. \tag{5}$$

With this, Eq. (2) reduces to

$$\langle F \rangle = (1/\Omega^*) \int_{\mathrm{BZ}^*} d^3q\, F^*(\mathbf{q}), \tag{6}$$

where Ω^* is the **q**-space volume of the BZ. The star is used to designate the **q**-space analogues of quantities whose basic definitions are given in terms of **k**-space. In particular, $F^*(\mathbf{q}) = F(2\pi\mathbf{q}/a) = F(\mathbf{k})$. The **q**-space analogue of the BZ of the fcc lattice, which is labeled BZ*, is the region such that

$$|q_x| \leqslant 1, |q_y| \leqslant 1, |q_z| \leqslant 1, \text{ and } |q_x| + |q_y| + |q_z| \leqslant (3/2), \tag{7}$$

where $\mathbf{q} = (q_x, q_y, q_z)$. The volume of this region is $\Omega^* = 4$. Our problem is to approximate the integral in Eq. (6) by a sum of the form

$$\langle F \rangle = \sum_{\mathbf{q}} w(\mathbf{q}) F^*(\mathbf{q}), \tag{8}$$

where the sum is over a discrete set of sampling points **q**, each of which has a weight factor $w(\mathbf{q})$ associated with it. Because of the factor $(1/\Omega^*)$ in Eq. (6), one has

$$\sum_{\mathbf{q}} w(\mathbf{q}) = 1. \tag{9}$$

2. Uniform Mesh Method (UMM)

The basic UMM integration formula for the fcc lattice is

$$\langle F \rangle = M^{-3} \sum_{a,b,c}{}' [m_{abc} u(M - a)\, u((3M/2) - a - b - c)]\, F^*(\mathbf{q}_{abc}), \tag{10}$$

where

$$\mathbf{q}_{abc} = (q_x, q_y, q_z) = (1/M)(a, b, c), \tag{11}$$

$$u(x) = \begin{cases} 1, & \text{if } x > 0, \\ \frac{1}{2}, & \text{if } x = 0, \\ 0, & \text{if } x < 0, \end{cases} \tag{12}$$

and

$$m_{abc} = 2^{Z(a,b,c)} P(a, b, c), \tag{13}$$

where $Z(a, b, c)$ is the number of nonzero elements in the set (a, b, c) and $P(a, b, c)$ is the number of distinct permutations of the set. The parameter M is a positive integer. The sum in Eq. (10) is over those integer values of a, b, and c such that:

$$a, b, \text{ and } c \text{ are either all even or all odd integers;} \tag{14a}$$

$$M \geqslant a \geqslant b \geqslant c \geqslant 0; \tag{14b}$$

$$a + b + c \leqslant (3M/2). \tag{14c}$$

Restriction (14a) leads to a bcc lattice of sampling points in $\mathbf{q}$-space, while restrictions (14b) and (14c) assure that only points in the irreducible 1/48-th of BZ are included in the sum. The function m_{abc} accounts for the number of equivalent points in the BZ, i.e., the number of points at which the integrand has the same value as at $\mathbf{q}_{abc}$ because of the symmetry properties (3). The product of unit step functions in Eq. (10) assigns a reduced weight to the sampling points that are on the surface of the BZ.

When $M = 10$, 20, or 40, the number of distinct (i.e., inequivalent) points at which the integrand is sampled is 48, 262, or 1686, respectively (these numbers include the sampling point at the exact center of the BZ). The *total* number of points sampled in the BZ, independent of whether the points are equivalent or not, is 10^3, 20^3, or 40^3, respectively.

Error Estimate

In essence the UMM replaces the integration over the BZ by a sum of integrations over small "subzones," each of which has the shape of a scaled-down BZ. The $\mathbf{q}$-space volume of these subzones is $\Omega^*_{\mathrm{SZ}} = (\Omega^*/M^3) = (4/M^3)$. The centers of these subzones form the bcc lattice of sampling points defined by Eqs. (11) and (14a). (Remember, the BZ of the fcc lattice has the same shape as the Wigner–Seitz cell of the bcc lattice.) A subzone contains all parts of $\mathbf{q}$-space closer to the sampling point at its center than to any other sampling point, so that each sampling point is at the geometric center (or center of mass) of the subzone associated with it. Thus, Eq. (6) is equivalent to

$$\langle F \rangle = (1/\Omega^*) \sum_{a,b,c} \int_{\mathrm{SZ}^*_{abc}} d^3q\, F^*(\mathbf{q}), \tag{15}$$

where each integral in the sum is over a different subzone. The subzone centered about the sampling point $\mathbf{q}_{abc}$ is labeled SZ^*_{abc}.

By expanding the $\mathbf{q}$-dependence of the integrand for each subzone in a Taylor series of powers of $(\mathbf{q} - \mathbf{q}_{abc})$ one obtains

$$F^*(\mathbf{q}) = F^*(\mathbf{q}_{abc}) + \nabla_{\mathbf{q}} F^*(\mathbf{q}_{abc}) \cdot (\mathbf{q} - \mathbf{q}_{abc}) + \tfrac{1}{2} \sum_{i,j} (\partial^2 F^*/\partial q_i\, \partial q_j)|_{\mathbf{q}=\mathbf{q}_{abc}} (\mathbf{q} - \mathbf{q}_{abc})_i\, (\mathbf{q} - \mathbf{q}_{abc})_j + \cdots, \tag{16}$$

where the subscripts i and j designate vector components in the x, y, or z direction. The substitution of this into Eq. (15) gives

$$\langle F \rangle = (\Omega^*_{\mathrm{SZ}}/\Omega^*) \sum_{a,b,c} F^*(\mathbf{q}_{abc}) + \tfrac{1}{2}(\Omega^*_{\mathrm{SZ}}/\Omega^*) \sum_{a,b,c} \nabla_{\mathbf{q}}{}^2 F^*(\mathbf{q}_{abc}) \Delta + \cdots, \tag{17}$$

where

$$\int_{SZ^*_{abc}} d^3q(\mathbf{q} - \mathbf{q}_{abc})_i (\mathbf{q} - \mathbf{q}_{abc})_j = \Omega^*_{SZ} \delta_{ij} \Delta. \tag{18}$$

Equation (18) defines Δ, which has the same value for all subzones. δ_{ij} is the Kronecker delta function. Since $\mathbf{q}_{abc}$ is at the geometric center of the subzone, the integral over SZ^*_{abc} of $(\mathbf{q} - \mathbf{q}_{abc})$ is zero, which causes the contribution to Eq. (17) of the linear term in Eq. (16) to be zero.

After full account is taken of the symmetries (3) and the periodicity (4), the first term on the right-hand side of Eq. (17) becomes the UMM integration formula, Eq. (10). The second term on the right-hand side of Eq. (17) gives an estimate of the error that results from the use of this integration formula. This error will be small if $F^*(\mathbf{q})$ is a smooth function of $\mathbf{q}$. However, if $F(\mathbf{q})$ is not smooth, particularly if it contains discontinuities or singularities, the contribution to Eq. (17) of the second and other higher order terms on its right-hand side may be quite large, so that significant error could result from neglecting them.

Some of the subzones near the surface of the BZ are truncated by the surface of the BZ. The reduced contributions of such subzones are accounted for in the UMM by the product of unit step functions in Eq. (10). This accounting procedure is possible in the UMM, since the part of any truncated subzone that is outside the region of integration is equivalent, because of Eqs. (3) and (4), to the part of some other truncated subzone that is within the BZ.

The value of Δ for the bcc lattice of sampling points of the UMM is $(19/96M^2)$. For comparison, consider the sc lattice of sampling points that would result from letting a, b, and c in Eq. (11) by *any* set of integers, and not just the sets that satisfy restriction (14a). Equations (17) and (18) would still be valid. However, the number of terms in the sum in Eq. (17) would be four times greater than when restriction (14a) is used, and the value of (Ω^*_{SZ}/Ω^*) would be 1/4 as large. The value of Δ would be $(1/12M^2)$ for the cube-shaped subzones that result. This is less than the value of Δ for the bcc lattice of sampling points by a factor of $(8/19) = 0.42$. Consequently, the sc lattice of sampling points would reduce the error by a factor of 0.42 at the cost of increasing the number of sampling points by a factor of 4. This same reduction in error could be obtained with a bcc lattice of sampling points by increasing the value of M used by approximately $(19/8)^{1/2} = 1.54$, which would increase the number of sampling points by the slightly smaller factor of $(1.54)^3 = 3.66$.

3. Concentric Region Method (CRM)

fcc Brillouin Zone

In the CRM the BZ is divided into N distinct concentric regions by surfaces that have the shape of the surface of a scaled-down BZ. Let the symbols $R^{(\alpha)}$ with

$\alpha = 1, 2, \ldots$, and N designate the different regions. Let $R^{(1)}$ designate the region between the surface of the BZ and the largest BZ-shaped dividing surface; let $R^{(2)}$ designate the region between the inner surface of $R^{(1)}$ and the next largest BZ-shaped dividing surface, etc. The surface separating $R^{(\alpha)}$ from $R^{(\alpha+1)}$ has linear dimensions that are scaled down from those of the surface of the BZ by a factor of $(m/M)^{\alpha}$, where m and M are positive integers and $m < M$. Thus, the dimensions of $R^{(\alpha+1)}$ are less than those of $R^{(\alpha)}$ by a factor of m/M. A bcc lattice of sampling points is used in each region. The distance between sampling points is reduced from region to region by the same factor as the dimension of the region, so that all regions have the same number of sampling points (except the innermost region $R^{(N)}$). The decrease in the dimensions of the regions with increasing α produces the desired increase in the sampling density towards the zone center.

The basic CRM integration formula is

$$\langle F \rangle = \sum_{\alpha=1}^{N} \sum_{a,b,c}^{(\alpha)} w_{abc}^{(\alpha)} F^*(\mathbf{q}_{abc}^{(\alpha)}), \tag{19}$$

where

$$\mathbf{q}_{abc}^{(\alpha)} = (q_x, q_y, q_z) = (m^{\alpha-1}/M^{\alpha})(a, b, c) \tag{20}$$

and

$$w_{abc}^{(\alpha)} = (m^{\alpha-1}/M^{\alpha})^3 m_{abc} f_{abc}, \tag{21}$$

where $\sum_{abc}^{(\alpha)}$ designates a sum over the sampling points in region $R^{(\alpha)}$, and the function m_{abc} is given by Eq. (13). The function f_{abc} gives the fraction of the volume of the subzone surrounding the point $q_{abc}^{(\alpha)}$ that is within the region $R^{(\alpha)}$. The weight factors $w_{abc}^{(\alpha)}$ are such that

$$\sum_{a,b,c}^{(\alpha)} w_{abc}^{(\alpha)} = (m/M)^{3(\alpha-1)} [1 - (m/M)^3] \qquad (\text{for } \alpha < N), \tag{22}$$

$$\sum_{a,b,c}^{(N)} w_{abc}^{(N)} = (m/M)^{3(N-1)} \qquad (\text{for } \alpha = N), \tag{23}$$

and

$$\sum_{\alpha=1}^{N} \sum_{a,b,c}^{(\alpha)} w_{abc}^{(\alpha)} = 1. \tag{24}$$

Just as in the UMM, a subzone is the BZ-shaped region around each regularly placed sampling point that contains all parts of $\mathbf{q}$-space closer to the sampling

point in question than to any other sampling point. However, some of the subzones are truncated by the surfaces of the regions $R^{(\alpha)}$. For example, consider the outermost region $R^{(1)}$. Its outer surface is made up of segments of the $2 + 2 + 2 + 8 = 14$ planes defined by the equal signs in Eq. (7); its inner surface is made up of segments of the 14 planes defined by $|q_x| = (m/M)$, $|q_y| = (m/M)$, $|q_z| = (m/M)$, and $|q_x| + |q_y| + |q_z| = (3m/2M)$. Some of the truncated subzones in $R^{(1)}$ are intersected by only one of these $14 + 14 = 28$ planes, while some are truncated by two of these planes. To assure that none of the subzones is truncated by more than 2 of these 28 planes, only values of m and M that are equal to

$$4(\text{integer}) + 1 = 5, 9, 13, 17, 21... \tag{25}$$

are considered. One can show that, when m and M have these values, the "corners" (see point W in Fig. 1) of the outer and inner surfaces of the region are always coincident with a corner of one of the subzones. This eliminates the possibility of any subzone being truncated by three (or more) of these planes.

The contribution to $\langle F \rangle$ of a truncated subzone is given by the integral of $F^*(\mathbf{q})$ over the part of the subzone that is within the region with which the subzone is associated. To best approximate this, the value of the integrand $F^*(\mathbf{q})$ is sampled at the point at the geometric center of the part of the subzone that is inside the region, and the weight is reduced from that of an untruncated subzone by the fraction f_{abc}.

If an expansion similar to Eq. (17) were made of the integral over a region $R^{(\alpha)}$, the location just specified for the sampling points at the surface of the region would be such that the contribution to the integral of the first derivative terms in the Taylor series would be identically zero for the surface subzones, as well as for the interior subzones. In this way, the error that results from the use of CRM integration formula (18) is minimized.

There are two basic types of regions: Type I and Type II. Regions $R^{(1)}$ through $R^{(N-1)}$ are of Type I and have the shape of a scaled-down BZ with a smaller BZ-shaped region absent from the center. Region $R^{(N)}$ is of Type II, it has the shape of a scaled down BZ and includes the region at its center.

The different kinds of subzones that exist in a Type I region are given below, along with the value of the fraction f_{abc} and the values of a, b, and c that determine the sampling points $q_{abc}^{(\alpha)}$. (Only sampling points from 1/48-th of each region are needed, since the function m_{abc} accounts for the contributions of the subzones in the other parts of the region.)

Ia. The subzones truncated by the outer [1, 0, 0] surface of the region have $f_{abc} = (1/2)$ and

$$(a, b, c) = (M - (35/96), b, c), \tag{26a}$$

where

$$b + c < (1/2)(M - 1) \qquad \text{and} \quad b \geqslant c > 0; \tag{26b}$$

b and c are odd integers.

Ib. The subzones truncated by the outer [1, 0, 0] and [1, 1, 1] surfaces have $f_{abc} = (7/16)$ and

$$(a, b, c) = (M - (11/28), b' - (23/336), c' - (23/336)), \tag{27a}$$

where

$$b' + c' = (1/2)(M - 1) \qquad \text{and} \quad b' \geqslant c' > 0; \tag{27b}$$

b' and c' are odd integers.

Ic. The subzones with centers inside $R^{(\alpha)}$ that are truncated by the outer [1, 1, 1] surface have $f_{abc} = (17/24)$ and

$$(a, b, c) = (a' - (35/272), b' - (35/272), c' - (35/272)), \tag{28a}$$

where

$$a' + b' + c' = (3M/2) - (1/2) \qquad \text{and} \quad M - 1 > a' \geqslant b' \geqslant c' > 0; \tag{28b}$$

a', b', and c' are odd integers.

Id. The subzones with centers outside $R^{(\alpha)}$ that are truncated by the outer [1, 1, 1] surface have $f_{abc} = (7/24)$ and

$$(a, b, c) = (a' - (5/16), b' - (5/16), c' - (5/16)), \tag{29a}$$

where

$$a' + b' + c' = (3M/2) + (1/2) \qquad \text{and} \quad M > a' \geqslant b' \geqslant c' > 0; \tag{29b}$$

a', b', and c' are even integers.

Ie. The subzones truncated by the outer [1, 1, 1] and [1, 1, -1] surfaces have $f_{abc} = (1/8)$ and

$$(a, b, c) = (a' - (23/48), b' - (23/48), 0) \tag{30a}$$

where

$$a' + b' = (3M/2) + (1/2) \qquad \text{and} \quad M > a' \geqslant b' > (1/2)(M + 1); \tag{30b}$$

a' and b' are even integers.

If. The subzones contained entirely within $R^{(\alpha)}$ have $f_{abc} = 1$. The numbers a, b, and c for these subzones take on all integer values such that:[1]

$$a, b, \text{ and } c \text{ are either all even or all odd integers;} \tag{31a}$$

$$a \geqslant b \geqslant c \geqslant 0; \tag{31b}$$

$$a + b + c \leqslant (3/2)(M - 1); \tag{31c}$$

$$\begin{cases} \text{either } M - 1 \geqslant a \geqslant m + 1, \\ \text{or } m \geqslant a \geqslant (1/2)(m + 1) \text{ and } a + b + c \geqslant (3/2)(m + 1). \end{cases} \tag{31d}$$

Ig. The subzones truncated by the inner [1, 0, 0] surface of the region have $f_{abc} = (1/2)$ and

$$(a, b, c) = (m + (35/96), b, c), \tag{32a}$$

where

$$b + c < (1/2)(m - 1) \quad \text{and} \quad b \geqslant c > 0; \tag{32b}$$

b and c are odd integers.

Ih. The subzones truncated by the inner [1, 0, 0] and [1, 1, 1] surfaces have $f_{abc} = (9/16)$ and

$$(a, b, c) = (m + (11/36), b' + (23/432), c' + (23/432)), \tag{33a}$$

where

$$b' + c' = (1/2)(m - 1) \text{ and } b' \geqslant c' > 0; \tag{33b}$$

b' and c' are odd integers.

Ii. The subzones with centers outside $R^{(\alpha)}$ that are truncated by the inner [1, 1, 1] surface have $f_{abc} = (7/24)$ and

$$(a, b, c) = (a' + (5/16), b' + (5/16), c' + (5/16)), \tag{34a}$$

where

$$a' + b' + c' = (3m/2) - (1/2) \quad \text{and} \quad m - 1 > a' \geqslant b' \geqslant c' > 0; \tag{34b}$$

a', b', and c' are odd integers.

Ij. The subzones with centers inside $R^{(\alpha)}$ that are truncated by the inner [1, 1, 1] surface have $f_{abc} = (17/24)$ and

$$(a, b, c) = (a' + (35/272), b' + (35/272), c' + (35/272)), \tag{35a}$$

[1] Restriction (31d) can also be stated as follows: $M - 1 \geqslant a \geqslant (1/2)(m + 1)$ and, if $a \leqslant m$, exclude values of a, b, and c for which $a + b + c < (3/2)(m + 1)$.

where

$$a' + b' + c' = (3m/2) + (1/2) \quad \text{and} \quad m > a' \geqslant b' \geqslant c' > 0; \tag{35b}$$

a', b', and c' are even integers.

Ik. The subzones truncated by the inner [1, 1, 1] and [1, 1, −1] surfaces have $f_{abc} = (7/8)$ and

$$(a, b, c) = (a' + (23/336), \quad b' + (23/336), \quad 0), \tag{36a}$$

where

$$a' + b' = (3m/2) + (1/2) \quad \text{and} \quad m > a' \geqslant b' > (1/2)(m + 1); \tag{36b}$$

a' and b' are even integers.

The different kinds of subzones that exist in a Type II region, and the values of f_{abc} and of a, b, and c are given below:

IIa through IIe. These are the same as Ia through Ie, respectively.

IIf. The subzones contained entirely within $R^{(\alpha)}$ have $f_{abc} = 1$. The quantities a, b, and c for these subzones have all integer values such that:

$$a, b, \text{ and } c \text{ are either all even or all odd integers;} \tag{37a}$$

$$a \geqslant b \geqslant c \geqslant 0; \tag{37b}$$

$$a + b + c \leqslant (3/2)(M - 1); \tag{37c}$$

$$M - 1 \geqslant a > 0. \tag{37d}$$

IIg. The subzone at the center can be accounted for with the following values for a, b, and c and for the product $m_{abc}f_{abc}$:

$$(a, b, c) = (0.2, 0.0, 0.0), \qquad m_{abc}f_{abc} = (10/35); \tag{38a}$$

$$(a, b, c) = (1/2)^{1/2}\,(0.2, 0.2, 0.0), \qquad m_{abc}f_{abc} = (16/35); \tag{38b}$$

$$(a, b, c) = (1/3)^{1/2}\,(0.2, 0.2, 0.2), \qquad m_{abc}f_{abc} = (9/35). \tag{38c}$$

It is often difficult to determine the value of the integrands at the point $\mathbf{q} = 0$, which is at the exact center of the BZ. Because of this, the contribution to $\langle F \rangle$ of the subzone surrounding $\mathbf{q} = 0$ has been determined by averaging the value of the integrand over the surface of a small sphere centered at $\mathbf{q} = 0$. The three sampling points given in IIg, which determine the contribution of this subzone, were obtained by using Houston's approximation to do the averaging over this sphere [3]. We have found $|\,\mathbf{q}\,| = 0.2\,(m^N/M^{N+1})$ to be a convenient value for the

TABLE I

Values of a, b, and c and of m_{abc} and f_{abc} for regions of Type I when $M = 17$ and $m = 9$

(The 110 distinct sets of values for a, b, and c for subzones of kind IIf are not given, since they are easily determined with the algorithm (31a)–(31d) given in the text.)

Kind of subzone	a ,	b ,	c	m_{abc}	f_{abc}
Ia	16 + (61/96) ,	1 ,	1	24	1/2
	16 + (61/96) ,	3 ,	1	48	1/2
	16 + (61/96) ,	3 ,	3	24	1/2
	16 + (61/96) ,	5 ,	1	48	1/2
Ib	16 + (17/28) ,	4 + (313/336),	2 + (313/336)	48	(7/16)
	16 + (17/28) ,	6 + (313/336),	0 + (313/336)	48	(7/16)
Ic	8 + (237/272),	8 + (237/272),	6 + (237/272)	24	(17/24)
	10 + (237/272),	6 + (237/272),	6 + (237/272)	24	(17/24)
	10 + (237/272),	8 + (237/272),	4 + (237/272)	48	(17/24)
	10 + (237/272),	10 + (237/272),	2 + (237/272)	24	(17/24)
	12 + (237/272),	6 + (237/272),	4 + (237/272)	48	(17/24)
	12 + (237/272),	8 + (237/272),	2 + (237/272)	48	(17/24)
	12 + (237/272),	10 + (237/272),	0 + (237/272)	48	(17/24)
	14 + (237/272),	4 + (237/272),	4 + (237/272)	24	(17/24)
	14 + (237/272),	6 + (237/272),	2 + (237/272)	48	(17/24)
	14 + (237/272),	8 + (237/272),	0 + (237/272)	48	(17/24)
Id	9 + (11/16) ,	7 + (11/16) ,	7 + (11/16)	24	(7/24)
	9 + (11/16) ,	9 + (11/16) ,	5 + (11/16)	24	(7/24)
	11 + (11/16) ,	7 + (11/16) ,	5 + (11/16)	48	(7/24)
	11 + (11/16) ,	9 + (11/16) ,	3 + (11/16)	48	(7/24)
	11 + (11/16) ,	11 + (11/16) ,	1 + (11/16)	24	(7/24)
	13 + (11/16) ,	5 + (11/16) ,	5 + (11/16)	24	(7/24)
	13 + (11/16) ,	7 + (11/16) ,	3 + (11/16)	48	(7/24)
	13 + (11/16) ,	9 + (11/16) ,	1 + (11/16)	48	(7/24)
	15 + (11/16) ,	5 + (11/16) ,	3 + (11/16)	48	(7/24)
	15 + (11/16) ,	7 + (11/16) ,	1 + (11/16)	48	(7/24)

Table continued

TABLE I (*continued*)

Kind of subzone	a ,	b ,	c	m_{abc}	f_{abc}
Ie	13 + (25/48) ,	11 + (25/48) ,	0	24	(1/8)
	15 + (25/48) ,	9 + (25/48) ,	0	24	(1/8)
If	—	—	—	—	1
Ig	9 + (35/96) ,	1 ,	1	24	1/2
Ih	9 + (11/36) ,	3 + (23/432) ,	1 + (23/432)	48	(9/16)
Ii	5 + (5/16) ,	5 + (5/16) ,	3 + (5/16)	24	(7/24)
	7 + (5/16) ,	3 + (5/16) ,	3 + (5/16)	24	(7/24)
	7 + (5/16) ,	5 + (5/16) ,	1 + (5/16)	48	(7/24)
Ij	6 + (35/272) ,	4 + (35/272) ,	4 + (35/272)	24	(17/24)
	6 + (35/272) ,	6 + (35/272) ,	2 + (35/272)	24	(17/24)
	8 + (35/272) ,	4 + (35/272) ,	2 + (35/272)	48	(17/24)
Ik	8 + (23/336) ,	6 + (23/336) ,	0	24	(7/8)

radius of this sphere. Note that the sum of the effective values for the product $m_{abc}f_{abc}$ given in Eq. (38) is 1, as it must be, since $m_{abc} = 1$ for $a = b = c = 0$ and $f_{abc} = 1$ for an untruncated subzone.

When values for M and m are being chosen, a compromise must be made between the conflicting demands for accuracy and for computational efficiency. A choice that we have found to be useful is $M = 17$ and $m = 9$. For reference, the values of a, b, and c, of m_{abc}, and of f_{abc} for Type I regions when $M = 17$ and $m = 9$ are given in Table I. When $M = 17$ and $m = 9$, there are 147 distinct sampling points in a Type I region and 179 distinct sampling points in a Type II region, so that the total number of distinct sampling points when N regions are used is $147^{N-1} + 179$.

sc Brillouin Zone

With a little modification, the CRM for evaluating integrals over the BZ of the fcc lattice can be extended so that it is also useful for evaluating integrals over the cubic BZ of the *sc* lattice. First, the relationship between the dimensionless variable $\mathbf{q}$ and the wave vector $\mathbf{k}$ must be redefined so that the $\mathbf{q}$-space analogue of

the surface of the cubic BZ of the sc lattice is made up of segments of the six planes $|q_x| = 1$, $|q_y| = 1$, and $|q_z| = 1$. This **q**-space cube is then divided into several concentric regions by surfaces that have the shape of the surface of the BZ of the fcc lattice. Let $R^{(1)}$ designate the region between the **q**-space analog of the surface of the BZ and the largest dividing surface; let $R^{(2)}$ designate the region between the inner surface of $R^{(1)}$ and the next largest dividing surface, etc. The resulting integration formula has exactly the form of Eq. (19) and the points $\mathbf{q}_{abc}^{(\alpha)}$ are given by Eq. (20). However, Eq. (21) for $w_{abc}^{(\alpha)}$ must be altered by the insertion of a factor of 1/2 on its right-hand side to account for the fact that the **q**-space volume of the BZ of the sc lattice is $\Omega^* = 8$, not 4 as with the fcc lattice. The only other important change is that the outermost region $R^{(1)}$ is of a new type, which we will call Type III. Regions $R^{(2)}$ through $R^{(N-1)}$ are of Type I, and $R^{(N)}$ is of Type II.

The different kinds of subzones that exist in a Type III region and the values of f_{abc} and of a, b, and c are given below.

IIIa. The subzones contained entirely within the region and those truncated by the outer surface of the region have

$$f_{abc} = u(M - a)\, u(M - b)\, u(M - c), \tag{39}$$

where the unit step function $u(x)$ is defined by Eq. (12). The numbers a, b, and c for these subzones take on all integer values such that:

$$a, b, \text{ and } c \text{ are either all even or all odd integers;} \tag{40a}$$

$$a \geqslant b \geqslant c \geqslant 0; \tag{40b}$$

$$\begin{cases} \text{either } M \geqslant a \geqslant m + 1, \\ \text{or } m \geqslant a \geqslant (1/2)(m + 1) \quad \textit{and } a + b + c \geqslant (3/2)(m + 1). \end{cases} \tag{40c}$$

IIIb through IIIf. These are the same as Ig through Ik, respectively.

Since only the outermost region $R^{(1)}$ can be of Type III, a Type III region always has its outer surface coincident with the surface of the BZ, so that the exterior part of any subzone that is truncated by the outer surface of the region is equivalent because of Eqs. (3) and (4) to the part of the same other truncated subzone that is inside the BZ. Because of this, the reduced contributions of these truncated subzones can be accounted for by the values of f_{abc} specified by Eq. (39).

4. Gaussian Method (GM)

The Gaussian method is based on Gauss' formula [4]

$$\int_{-1}^{+1} f(x)\, dx = \sum_{i=1}^{n} w_i f(x_i) + R_n\,. \tag{41}$$

Here, the abscissa x_i is the i-th root of the Legendre polynomial $P_n(x)$, and the weight factors are $w_i = 2/(1 - x_i)^2 [P_n'(x_i)]^2$. When the positive integer n is even, $n/2$ of the abscissa are positive, and each of the remaining abscissas is equal to the negative of one of the positive abscissas. Both $\pm | x_i |$ have the same weight factor. The abscissas are most dense near the limits of the interval of integration.

To apply Eq. (41) to the three-dimensional integration over the BZ of the fcc lattice, one extends the region of integration to include the entire cube contained within the six planes $| q_x | = 1$, $| q_y | = 1$, and $| q_z | = 1$. The periodicity (4) is used to determine the values of integrand in the part of this cube that is outside the first BZ. To cause the maximum in the sampling density to be at the zone center and at the corners of our cube, which are equivalent points, one applies Gauss' formula to the part of the cube in which each of the components q_x, q_y, and q_z is positive. (This part of the cube is also *a* cube.) Then, using the symmetry property (3) and neglecting the remainder term R_n, one obtains the basic GM integration formula:

$$\langle F \rangle = (1/4) \sum_{i=1}^{n} \sum_{j=1}^{i} \sum_{l=1}^{j} [u((3/2) - q_i - q_j - q_l)\, m'_{ijl} w_i w_j w_l]\, F^*(\mathbf{q}_{ijl}), \tag{42}$$

where

$$m'_{ijl} = \begin{cases} 6, & \text{if } i > j > l, \\ 3, & \text{if } i > j = l \text{ or } i = j > l, \\ 1, & \text{if } i = j = l, \end{cases} \tag{43}$$

and

$$\mathbf{q}_{ijl} = (q_x, q_y, q_z) = (q_i, q_j, q_l), \tag{44}$$

where

$$q_i = (1/2)(1 + x_i), \tag{45}$$

and similarly for q_j and q_l. The x_i and w_i are the abscissas and weight factors in Eq. (41), and the subscripts are assumed to be such that $x_i < x_{i+1}$. The unit step function $u[(3/2) - q_i - q_j - q_l]$ accounts for the fact that, for each point q_{ijl} outside the first BZ, there is one point $q_{i'j'l'}$ inside the first BZ where the integrand has the same value, and vice-versa. By considering only even values of n, one can avoid the possibility of the argument of the unit step function being zero. The factor m_{ijl} and the indicated limits on the summations over i, j, and l account for the equivalence of sampling points that results from the symmetry properties (3).

For n = even, the number of distinct sampling points in the GM is equal to $(1/12)(n^3 + 3n^2 + 2n)$. For $n = 12$, $n = 16$, and $n = 20$, the numbers of distinct sampling points are 182, 408, and 770, respectively.

5. Comparison of Different methods

$$Q(\theta) = (30/\pi^5)(C(\theta)/\theta^3), \tag{46}$$

where

$$C(\theta) = (1/\Omega^*) \int_{BZ^*} d^3q \left[\frac{|\mathbf{q}|/\theta}{\sinh(|\mathbf{q}|/\theta)}\right]^2 \tag{47}$$

and

$$\theta = (ak_B/\pi\hbar v)\, T, \tag{48}$$

where θ is a generalized temperature, T is the absolute temperature, a is the lattice constant, k_B is Boltzmann's constant, $\hbar$ is (Planck's constant/2π), and v is the velocity of sound. $C(\theta)$ is proportional to the contribution of a single branch of the phonon disparsion relation to the specific heat in the Debye approximation.

The integrand in Eq. (47) possesses all of the properties that make the calculation of low-temperature values for C_V and $\gamma(T)$ difficult. In particular, the integrand tends to zero as $(|\mathbf{q}|/\theta) \to \infty$, and it tends to one as $(|\mathbf{q}|/\theta) \to 0$. It is equal to 1/2 when $(|\mathbf{q}|/\theta) \approx 1.5$. At high temperatures ($\theta \gg 1.5$), the integrand is essentially constant over the entire BZ, while at low temperatures ($\theta \ll 1$) the major contribution to the integral is from the region of $\mathbf{q}$-space near $\mathbf{q} = 0$. As θ decreases, $C(\theta)$ becomes proportional to θ^3, so that, for $\theta < 0.1$,

$$1 > Q(\theta) > 0.9997. \tag{49}$$

By comparing the value of $Q(\theta)$ obtained numerically with this analytic result, we can determine the accuracy of the integration method used.

The values of $Q(\theta)$ obtained with the different numerical methods for evaluating the integral over the BZ are given in Fig. 2. The numbers in parenthesis indicate the number of distinct points at which the value of the integrand is sampled. For example, these numbers give the number of different values of $\mathbf{q}$ at which the dynamical matrix would have to be diagonalized in a calculation of the specific heat C_V based on the complete phonon frequency spectrum $\omega_{\mathbf{k}s}$. (Here, s is a polarization index; for an alkali halide, $s = 1, 2, \ldots, 6$.)

The difference between the two UMM results with $M = 40$ in Fig. 2 is that the contribution of the sampling point at the exact center of the BZ (i.e., the point $\mathbf{q} = 0$) is included in the result obtained with 1686 distinct sampling points, while it is omitted in the result obtained with 1685 points. The large difference between these two UMM results clearly illustrates the special importance of the subzone at

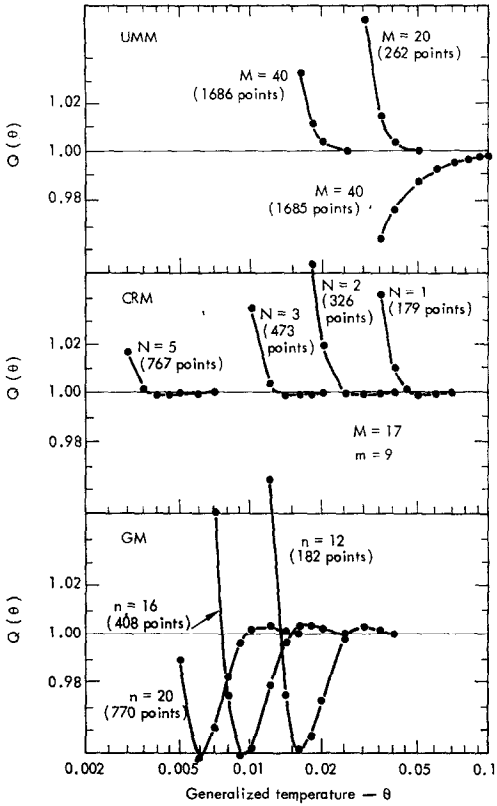

FIG. 2. The function $Q(\theta)$ as determined with the uniform mesh method (UMM), the concentric region method (CRM), and the Gaussian method (GM). The dots designate calculated values, and the numbers in parentheses give the number of distinct sampling points used in the calculation. Note that $\theta \sim (T/\theta_D)$, where θ_D is the Debye temperature.

the center of the BZ. The same type of sensitivity to the contribution of the subzone at the center also exists in the CRM. In fact, for both the UMM and CRM the lowest value of θ at which accurate results can be obtained is directly proportional to the linear dimensions of the subzone at the center of the BZ.

6. DISCUSSION

The advantage of increasing the density of sampling points towards the zone center is obvious from Fig. 2. For example, the UMM calculation involving 1686 distinct sampling points is little better at low temperatures than the CRM calcula-

tion involving only 326 points. Of course, the UMM calculation in principle gives more accurate results at high temperatures, but the increased accuracy is of no practical value.

Figure 2 also reveals that for $N \geqslant 3$ the CRM gives reliable low-temperature results with slightly fewer distinct sampling points than the GM. Nevertheless, the main advantage of the CRM over the GM is its greater flexibility. Once one has written a computer routine to evaluate integrals with the CRM integration formula,[2] one can alter the distribution of the sampling points within the BZ and/or the total number of sampling points simply by changing the values of the parameters N, M, and m. This flexibility can be useful both for verifying that the results obtained are not sensitive to the sampling used and for adjusting the sampling to obtain the greatest possible computational efficiency.

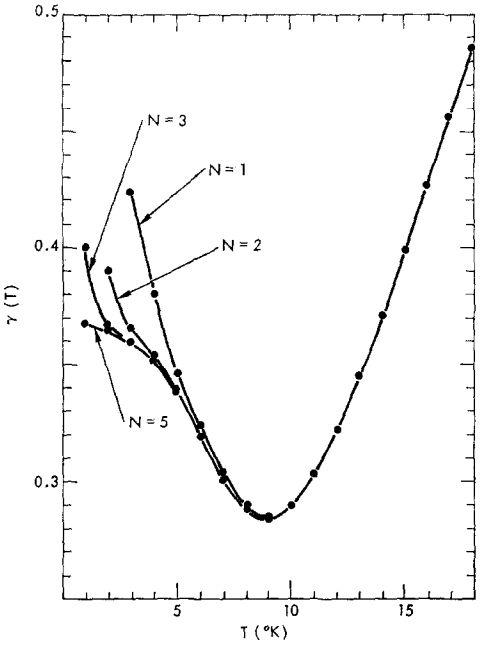

FIG. 3. The macroscopic Grüneisen function $\gamma(T)$ for KBr as calculated with the CRM with different numbers of regions N and with $M = 17$ and $m = 9$.

[2] Note to programmer: Despite the several different kinds of truncated subzones listed in Section 3, the CRM integration formula is not difficult to program. A convenient way to check a program is to verify that Eqs. (22), (23), and (24) are satisfied and that the results given in Table I are reproduced when $M = 17$ and $m = 9$. It must be remembered that the formulas in Section 3 are valid only when m and M are two of the integers given by Eq. (25).

As an example of an application of the CRM, we show in Fig. 3 the results of a calculation of the macroscopic Grüneisen function $\gamma(T)$ for KBr, where

$$\gamma(T) = \left[\sum_s \int_{BZ} d^3k \; C_{\mathbf{k}s}(T)\,\gamma_{\mathbf{k}s}\right]\left[\sum_s \int_{BZ} d^3k \; C_{\mathbf{k}s}(T)\right]^{-1}. \tag{50}$$

Here $C_{\mathbf{k}s}(T)$ is the heat capacity of the normal mode with wave vector $\mathbf{k}$ and polarization index s, and $\gamma_{\mathbf{k}s}$ is the associated mode-Grüneisen parameter. The details of this calculation are given in a recent article by Hardy and Karo [5]. Heretofore, there had been some doubt concerning whether or not the theoretical values for $\gamma(T)$ passed through a minimum at low temperatures [6]. By using the CRM we were able to show unambiguously that a pronounced minimum in $\gamma(T)$ is predicted by the anharmonic deformation dipole model (results shown in Fig. 3), but that no minimum is predicted by the rigid ion model (result not shown here).

Because of the parameter $\gamma_{\mathbf{k}s}$, the integrand in the numerator of Eq. (50) does not have a unique limiting value as $\mathbf{k} \to 0$, but has different limiting values in different directions. This is the type of singular behavior at the center of the BZ that led us in Section 3 to specify the use of the average value given by (38) when determining the contribution to $\langle F \rangle$ of the subzone at the center of the BZ. The rather good low-temperature approximation to $\gamma(T)$ that was obtained with only one region (see the $N = 1$ curve in Fig. 3) is due, to a large extent, to the use of this method for determining the contribution of the subzone at the center. Nevertheless, this method, which works well when calculating $\gamma(T)$ and C_V, may not be the best method when other properties are being calculated. The method of estimating the contribution of the subzone at the center should be adjusted to account for the particular properties near $\mathbf{q} = 0$ of the integrands involved in the problem being considered.

A comparison of Figs. 2 and 3 suggests that the information in Fig. 2 can be roughly related to the calculation of the low-temperature properties of real crystals by identifying the parameter θ with the ratio (T/θ_D), where θ_D is the Debye temperature of the crystal being considered. (The value of θ_D for KBr is 174°K [7].)

Finally, it should be noted that the type of problem for which the CRM integration formula is useful is quite different from the type of problem discussed by Gilat and collaborators [8]. They have been primarily concerned with the problem of calculating properties such as the density of states function $g(\omega)$ for which the CRM is unsuited. Usually, the contributions of the very long-wave-length normal modes to properties such as $g(\omega)$ are of relatively little interest. In contrast the CRM is specifically designed for calculating properties for which the contributions of these normal modes are of special interest.

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