9. The low-frequency limit of such masers is determined by the overlap of adjacent resonances.

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Lattice Specific Heats near 0°K with an Application to Germanium*

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Formulas for the low-temperature lattice specific heat are developed on the basis of the general adiabatic and harmonic assumptions, independently of special models or numerical procedures. Explicit simple formulas are obtained for $\theta_D(0)$, the equivalent Debye characteristic temperature at 0°K, and for the curvature of $\theta_D(T)$ at 0°K. Discussions are given of the resulting dependence of $\theta_D(0)$ on physical parameters and the significance of the formula for $\theta_D(0)$ as a check on the basic assumptions, of the absence of a linear term in $\theta_D(T)$, and of the dependence of the curvature on the dispersion of elastic waves. $\theta_D(0)$ is calculated for Ge as 374.0°K; an error of ± 2°K is estimated as due to errors in the elastic constants whereas the computational error is negligible. $\theta_D(T)$ is calculated for Ge for $[T/\theta_D(0)] < 0.11$ using two models. The first is a simple model of the frequency spectrum which gives results like typical force-constant models, and disagrees with measurement. The second is a model of the frequency spectrum based on the direct measurements by inelastic neutron scattering; this model shows much greater dispersion, and gives much better agreement of $\theta_D(T)$ with measurement.

I. INTRODUCTION AND SUMMARY

THE technique of low-temperature specific heat measurements now provides sufficient accuracy at temperatures low enough to permit reasonable extrapolation to 0°K in many cases. Accordingly, attention may be focused on the limiting behavior at 0°K, which is a point of particular simplicity for theoretical discussion, as will be shown below. The observed specific heat curves show substantial deviations from the Debye approximation rather close to 0°K, even for simple monatomic lattices. Considerable work has been devoted to explaining these deviations as properties of various microscopic models of the dynamics of crystal lattices, and conversely, successful explanations support the validity of these models and the assumptions underlying them.[1] Several workers have paid particular attention to the limiting behavior at 0°K. Blackman[1] has emphasized the occurrence of deviations from the limiting T^3 law at substantially lower temperatures than the Debye approximation would give, on the basis of calculations on various force constant models. Bhatia and Horton[2] discuss the limiting curvature of the equivalent Debye characteristic temperature, $\theta_D(T)$, at 0°K, and point out that $\theta_D(T)$ could curve upward although it usually curves downward.

Barron and Morrison[3] emphasize the importance of fitting specific heat data near 0°K, not only with terms in T^3 but also T^5 and T^7. Bhatia and Tauber, and Betts, Bhatia, and Wyman[4] have developed approximate methods for evaluating the limiting value of $\theta_D(T)$ at 0°K based on expansions in harmonic polynomials. (Older methods may be found in Blackman.[1]) Horton and Schiff[5] have applied similar approximate methods (refined somewhat) to the evaluation of the curvature of $\theta_D(T)$ at 0°K, and confirmed an upward curvature for a particular model of Pb. De Launay[6] has tabulated accurate values of $\theta_D(0)$ for cubic lattices over a range of elastic parameters and has also tabulated the curvature for a special force-constant model.

Most of the discussions of the low-temperature form of C_v or $\theta_D(T)$ in the above references, are complicated by the use of special force-constant models, or by special computational approximations, such as Houston's method.[2] In this paper we develop general expressions

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[1] For recent reviews with many illustrations of specific heat behavior see, for example, M. Blackman, in *Handbuch der Physik* (Springer-Verlag, Berlin, 1955), Vol. VII, Part I, p. 325; D. H. Parkinson, in *Reports on Progress in Physics* (The Physical Society, London, 1958), Vol. XXI, p. 226.

[2] A. B. Bhatia and G. K. Horton, Phys. Rev. **98**, 1715 (1955).

[3] T. H. K. Barron and J. A. Morrison, Can. J. Phys. **35**, 799 (1957).

[4] A. B. Bhatia and G. E. Tauber, Phil. Mag. **45**, 1211 (1954); Betts, Bhatia, and Wyman, Phys. Rev. **104**, 37 (1956).

[5] G. K. Horton and H. Schiff, Can. J. Phys. **36**, 1127 (1958).

[6] J. de Launay, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 2, p. 219.

for C_v and $\theta_D(T)$, independent of special models or methods of calculation. We emphasize that the formulation starts from three basic assumptions, believed to have wide validity: the adiabatic assumption, the harmonic assumption, and (to a more limited extent) the periodic assumption. The Debye approximation on which the representation $\theta_D(T)$ is based, is formulated in generalized form, without the assumption of isotropy. Thus it is exact in the limit $T \rightarrow 0°\text{K}$, under the three basic assumptions, and provides a very convenient theoretical reference point for discussion of the lattice heat capacity. Relations among measurable quantities which make no further assumptions provide a test of the basic assumptions. The relation for $\theta_D(0)$ in terms of elastic constants involves no microscopic information and so provides such a test. To bring this out and to simplify the computation of $\theta_D(0)$, a discussion is given of the form of that relation and of the nature and number of physical variables which determine $\theta_D(0)$. On the other hand, the curvature of $\theta_D(T)$ at 0°K is related to an average value of a microscopic quantity, the ratio of the first dispersion coefficient of the complete frequency spectrum (see Sec. II) to the fifth power of the corresponding sound velocity. This ratio is then averaged over direction and mode type. Measurement of the curvature thus provides values of this averaged microscopic quantity and is therefore a test of a particular microscopic model but not of the basic assumptions. We note briefly that the fact that $\theta_D(T)$ is parabolic at 0°K, with no linear term in T, is a general consequence of time-reversal symmetry of the equations of motion of the lattice.

Our discussion emphasizes the relationship between the specific heat and the complete frequency spectrum, and expresses relations in terms of integration over the Brillouin zone to sum over all vibration modes. No use is made of the density of modes in frequency, or frequency distribution function, as is usually done.

The general formulation is then applied to the interesting case of Ge, where recent work has partially determined the frequency spectrum, and standard force constant models fail to explain the measured behavior of the specific heat. The calculation of $\theta_D(T)$, its value and curvature at 0°K, are made by highly accurate numerical techniques, with no significant error for these purposes. $\theta_D(0)$ is found to be 374.0°K on the basis of recent low-temperature elastic-constant measurements, with a calculated error of ±2°K due only to errors in those measurements. This appears to be significantly different from existing measurements below 5°K, possibly corresponding to failure of the basic harmonic or adiabatic assumptions.[7] However, the measurements vary considerably from specimen to specimen, so additional measurements would be quite desirable.

$\theta_D(T)$ is then calculated for Ge on the basis of a simple model of the frequency distribution itself, which uses all the known structural and elastic-constant information. This model, referred to as the simple dispersion model (S.D.M.), introduces a typical or normal amount of dispersion into the elastic spectrum for waves in any direction, and has the correct $\theta_D(0)$. It gives a $\theta_D(T)$ typical of force-constant models, and disagrees significantly with the available measurements, by showing too shallow a minimum. The complete spectrum is then estimated by using the results of inelastic neutron scattering for the spectrum in certain directions. The approximation involved in this is justified by the dominance of the transverse [111] elastic modes whose spectrum has been measured, and shows much greater dispersion than the S.D.M. assumes or force-constant models would give. This model of the spectrum leads to a much deeper minimum in the $\theta_D(T)$ curve, in strikingly better agreement with the existing measurements. Calculation of the initial curvature is also made, and used to extrapolate the curve to 0°K, but no data exist to check it.

II. BASIC RELATIONS

Basic Assumptions and the General Heat Capacity Formula

The general model of the elastic and vibrational behavior of a solid used here, whose analysis leads to a precise description of the heat capacity, rests on three broad basic assumptions. These are: (1) the adiabatic assumption, which states that the lattice motion may be described entirely by the coordinates of the nuclei; (2) the harmonic assumption, which assumes the forces acting on nuclei displaced from equilibrium are proportional to the displacement; and (3) the periodic assumption, which assumes the lattice is periodic and satisfies periodic boundary conditions.[8]

Under the above assumptions the heat capacity at constant volume of the specimen may be written as a sum of oscillator heat capacities of a complete set of vibration modes in the form[9]

$$C_v = \sum_{i=1}^{r} \int_{\text{B.Z.}} \frac{K e^{x_i} x_i^2}{(e^{x_i}-1)^2} \frac{V}{(2\pi)^3} d^3k. \qquad (1)$$

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[7] After completion of this paper, new precise measurements of the specific heat of germanium (and silicon) by Flubacher, Leadbetter, and Morrison were kindly communicated to the authors in advance of publication through the courtesy of Dr. Morrison. These give a value for $\theta_D(0)$ of germanium of 374±2°K [Phil. Mag. 4, (1959)].

[8] The periodic boundary conditions are assumed for convenience in obtaining a simple description of the vibration modes. If surface effects are negligible, which is the case of interest here, this boundary condition is equivalent to any other, and is not a special restriction.

[9] A derivation of (1), with a discussion of the complete classification of vibration modes may be found, for example, in M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, Oxford, 1954), Chap. II, Eqs. (4.22), (6.24), and (6.25).

In (1), $x_i \equiv \hbar\omega_i(\mathbf{k})/KT$, $\omega_i(\mathbf{k})$ = the angular frequency of a normal vibration mode of wave number $\mathbf{k}$ (magnitude $2\pi/\lambda$, λ = wavelength), i = mode type number ($i=1$, 2, 3 for the acoustic modes; $i=4$ to r for the optical modes), K = Boltzmann's constant, $\hbar$ = Planck's constant over 2π, T = Kelvin temperature, V = volume of the specimen, and the integration is over the first Brillouin zone (B.Z. for short) or unit symmetrical cell in $\mathbf{k}$ space in which the mode density is $V/(2\pi)^3$. It is convenient to refer to the function $\omega_i(\mathbf{k})$, $i=1$ to r, $\mathbf{k}$ in the B.Z., as the *complete frequency spectrum* of the solid—to be distinguished from the density of states or frequency distribution function, which gives the number of states per unit frequency range, but is sometimes called the frequency spectrum.

Low-Temperature Expansions

At low temperatures, only small values of ω_i are important; otherwise x_i is large and the Einstein specific heat function, $Ke^{x_i}x_i^2/(e^{x_i}-1)^2$, is exponentially small. Hence only the acoustical modes, for which $\omega \rightarrow 0$ as $k \rightarrow 0$, contribute to C_v and we get an appropriate limiting form for C_v by assuming a series representation for $\omega_i(\mathbf{k})$, of which the first two terms are

$$\omega_i(\mathbf{k}) = v_i(\theta,\varphi)k[1-b_i(\theta,\varphi)k^2], \quad i=1,2,3. \tag{2}$$

In (2), $v_i(\theta,\varphi)$ is the sound velocity in the direction θ, φ, the direction of $\mathbf{k}$ (i.e., v_i is the velocity of long-wavelength elastic waves), k is the magnitude of $\mathbf{k}$, and $b_i(\theta,\varphi)$ is a measure of the first appearance of dispersion in the frequency spectrum at small k and will be called the *first dispersion coefficient.* The fact that (2) contains only odd powers of k is readily verified for all the lattice models referred to here, but is in fact a fundamental result, and follows from the time-reversal symmetry of the equations of motion. We assume (2) for the later development but a brief discussion of its basis is given in Appendix I.

Putting (2) into (1) now gives a general low-temperature expansion of the heat capacity, of which the first two terms are

$$\frac{C_v}{3NK} = \frac{V}{N}\left(\frac{KT}{\hbar}\right)^3 \frac{\pi}{90}\int_{4\pi} d\Omega \sum_{i=1}^{3} \frac{1}{v_i^3(\theta,\varphi)} + \frac{V}{N}\left(\frac{KT}{\hbar}\right)^5 \frac{10\pi^3}{63}\int_{4\pi} d\Omega \sum_{i=1}^{3} \frac{b_i(\theta,\varphi)}{v_i^5(\theta,\varphi)}. \tag{3}$$

In (3), the upper limit of integration for k has been made infinite, thus neglecting terms exponentially small compared to powers of T, and use has been made of the integral

$$\int_0^\infty \frac{x^{2n+2}e^x}{(e^x-1)^2}dx = (2n+2)!\,\zeta(2n+2), \tag{4}$$

where ζ is the Riemann zeta function:

$$\zeta(2n+2) \equiv \sum_{p=1}^{\infty} \frac{1}{p^{2n+2}};$$

$$\zeta(2)=\pi^2/6, \quad \zeta(4)=\pi^4/90, \quad \zeta(6)=\pi^6/945, \quad \text{etc.}$$

Also N, the number of nuclei in the specimen, has been introduced in each term, so that (3) gives the reduced (i.e., dimensionless) heat capacity per degree of freedom, a reduced specific heat.

Equation (3) as derived above is a precise formula as $T \rightarrow 0$°K, provided the three basic assumptions are satisfied. It is worth noting, however, that the periodic assumption is not really needed to establish (3), which holds in the limit in which only long waves are excited; hence the details of the lattice structure do not affect their behavior.[10]

Debye Approximation and the Equivalent Debye Theta Representation

A convenient representation of the specific heat uses the characteristic parameter of the Debye approximation. This approximation makes, in addition to the three basic assumptions above, the additional gross assumptions that the elastic waves show no dispersion, and that a single maximum frequency or frequency cutoff, ω_m, exists for modes of all types, in all directions. (However, elastic isotropy is not required.[11]) Only acoustical modes are considered, but the cutoff is chosen to provide the correct total number of degrees of freedom. Then using only the first term of (2) in (1), the angular and radial integrations separate, and putting the latter in terms of a reduced frequency variable x gives the approximate formula:

$$C_v \cong \frac{V}{(2\pi)^3}\left(\frac{KT}{\hbar}\right)^3 \left(\int_{4\pi} \sum_{i=1}^{3} \frac{1}{v_i^3(\theta,\varphi)} d\Omega\right) \times \int_0^{x_m} \frac{Ke^x x^4 dx}{(e^x-1)^2}; \tag{5}$$

$$x_m = \hbar\omega_m/KT \equiv \theta_D/T,$$

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[10] Equation (3) would be expected to hold for liquids or frozen disordered structures (e.g. glasses, alloys) at sufficiently low T. However, homogeneity on some scale smaller than the important wavelengths would be needed for the sound velocities to have meaning in (3) [strictly, this requires an infinite specimen in the limit 0°K, but for ordinary-sized homogeneous specimens there is a range of temperature which is close enough to 0°K for (3) to hold accurately but for which the inhomogeneity that is a consequence of finite size is still negligible]. The periodic assumption used above is convenient for classification of the modes, since it gives precise meaning to the quantum number $\mathbf{k}$ for all modes, but that the assumption is not needed is indicated by the fact that $\mathbf{k}$ has disappeared from (3). A justification of (3) for a nonperiodic material would introduce modes of definite $\mathbf{k}$ only for sufficiently long wavelengths, but we shall not need any extensions of this kind, and shall not pursue them here.

[11] The Debye approximation as defined above does not assume isotropy, as is usual but not necessary. Therefore it represents accurately the low-temperature behavior when only long waves are excited, and the solid behaves like an anisotropic continuum. This is the immediate answer to disprove Eucken's speculation that anisotropy causes deviations from the Debye approximation (see Blackman, reference 2, p. 363) which is answered rather indirectly by Blackman.

where θ_D is the characteristic parameter of the Debye theory, the Debye theta. If there are N nuclei participating, x_m or equivalently θ_D is fixed by putting the total number of modes equal to $3N$; hence

$$\frac{V}{(2\pi)^3}\left(\frac{KT}{\hbar}\right)^3\left(\int_{4\pi}\sum_{i=1}^{3}\frac{1}{v_i^3(\theta,\varphi)}d\Omega\right)\int_0^{x_m}x^2dx\equiv 3N. \tag{6}$$

Dividing (5) by (6) gives

$$\frac{C_v}{3NK}\cong\frac{3}{x_m^3}\int_0^{x_m}\frac{e^x x^4dx}{(e^x-1)^2}=3\left(\frac{T}{\theta_D}\right)^3 \times\int_0^{\theta_D/T}\frac{e^x x^4dx}{(e^x-1)^2}\equiv D(T/\theta_D). \tag{7}$$

We note the low-temperature form

$$C_v/3NK\cong D(T/\theta_D)=\tfrac{4}{5}\pi^4(T/\theta_D)^3+O(e^{-\theta_D/T}). \tag{8}$$

In (8), the only power appearing is T^3, and an approximation to $D(T/\theta_D)$ by this term alone holds within 0.7% for $T/\theta_D\leqslant 0.09$, which includes most of the region of interest in the discussion here.

Any specific heat curve may now be represented as a function of T by specifying an equivalent Debye theta as a function of T, $\theta_D(T)$, defined by

$$C_v/3NK\equiv D(T/\theta_D(T)), \tag{9}$$

where the function $D(x)$ is defined by (7). Comparing the representation (9), in the low-temperature form (8), with the general expansion (3), leads to an expansion of $\theta_D(T)$ in the form

$$\theta_D(T)=\theta_D(0)\left[1-C\left(\frac{T}{\theta_D(0)}\right)^2+\cdots\right]. \tag{10}$$

The parabolic form of (10), or absence of a term linear in T, is a consequence of the special form of (2) discussed above (i.e., odd powers of k only) leading to the special form of (3) (odd powers of T only). Thus the no-dispersion assumption for the elastic waves, $\omega_i(\mathbf{k})\cong v_i(\theta,\varphi)k$, holds especially well at small k, hence the Debye approximation holds especially well at low T, as shown by (10).

In (10)

$$\theta_D(0)=(6\pi^2)^{\frac{1}{3}}(\hbar/K)(N/V)^{\frac{1}{3}}v_0 I_3^{-\frac{1}{3}}; \tag{11a}$$

$$I_3=\frac{1}{12\pi}\int_{4\pi}d\Omega\sum_{i=1}^{3}\frac{1}{v_{ri}^3(\theta,\varphi)}. \tag{11b}$$

where the relative velocities $v_{ri}(\theta,\varphi)$ are defined b

$$v_{ri}(\theta,\varphi)=v_i(\theta,\varphi)/v_0, \tag{11c}$$

and v_0= an arbitrary reference velocity. Making the special choice $v_0=[c_{11}/\rho]^{\frac{1}{2}}$, where c_{11} is one of the elastic moduli, and ρ is the density, $\theta_D(0)$ may be written

$$\theta_D(0)=(6\pi^2)^{\frac{1}{3}}\frac{\hbar}{K}N_{\mathrm{Av}}^{\frac{1}{3}}\frac{c_{11}^{\frac{1}{2}}}{M^{\frac{1}{3}}\rho^{1/6}}I_3^{-\frac{1}{3}}, \tag{12}$$

where N_{Av}= Avogadro's number and $M=(\rho V/N)N_{\mathrm{Av}}$ = the average "molecular weight" of the atoms in the crystal. Similarly

$$C=\frac{100\pi^2}{21}(6\pi^2)^{\frac{2}{3}}\left(\frac{N}{V}\right)^{\frac{2}{3}}\frac{I_5}{I_3^{\frac{1}{3}}};$$

$$I_5=\frac{1}{12\pi}\int_{4\pi}d\Omega\sum_{i=1}^{3}\frac{b_i(\theta,\varphi)}{v_{ri}^5(\theta,\varphi)}. \tag{13}$$

Note that $\theta_D(0)$ is identical with the Debye parameter, when the latter is defined as above, since only the T^3 or continuum term remains in C_v as $T\rightarrow 0$°K, i.e., the Debye approximation as $T\rightarrow 0$°K is accurate.[11]

Discussion of Limiting Form of $\theta_D(T)$

The formula for $\theta_D(0)$, (11) or (12), is important in providing a precise relationship between two separately measured quantities. These are (1) the heat capacity (in the limit $T\rightarrow 0$°K) and (2) the elastic wave velocities $v_i(\theta,\varphi)$, $i=1, 2, 3$, which in turn depend on the elastic moduli and the density in a precisely known way. In addition the volume per atom, V/N, enters, or, equivalently, the mass per atom, M/N_{Av} (on introducing the density) as in the form (12). Equation (12) shows a simple dependence on c_{11}, M, and ρ, while the dimensionless integral I_3 is a function just of the ratios of elastic moduli; I_3 is a difficult function to calculate, but is well defined by (11b). An experimental test of (11) or (12) is then a test of the three basic assumptions mentioned above, since within these assumptions, the relation is exact.

Note that (11) seems to contain some microscopic description or model of the material, in that N, the number of atoms, enters, hence apparently (11) does not relate two purely macroscopic measurements. In fact this dependence on N, although convenient, is unnecessary, and of no significance, since N enters also in the formula for the specific heat per degree of freedom, which provides the other experimental way of determining $\theta_D(0)$; i.e., from (8)

$$\theta_D(0)=\left(\frac{4\pi^4}{5}\frac{3NKT^3}{C_v(T)}\right)^{\frac{1}{3}}.$$

A quantity for which there are two directly and independently measurable expressions is $\theta_D(0)N^{-\frac{1}{3}}$, or, equivalently, the intensive quantity $\theta_D(0)(V/N)^{\frac{1}{3}}$; the inverse cube of the latter, times T^3, is the heat capacity per unit volume (within a numerical factor). Actually N is a somewhat arbitrary quantity, since a consistent discussion of a material could be given in which two nuclei are counted as one unit, without altering (11). This would have physical justification if these nuclei were known to be much more tightly bound to each other than to the rest of the crystal.[12]

The coefficient C in (10) which measures the curvature of the reduced equivalent Debye theta curve $[\theta_D(T)/\theta_D(0)$ *vs* $T/\theta_D(0)]$, in contrast to $\theta_D(0)$ does depend in an intrinsic way on microscopic information or models. Thus (13) shows that C involves a particular, weighted average of the first dispersion coefficients $b_i(\theta,\varphi)$ $(i=1, 2, 3)$ over direction in the crystal. Microscopic information or models, such as force-constant models, are required to fix $b_i(\theta,\varphi)$. Conversely, measurement of the low-temperature specific heat provides a knowledge of that averaged microscopic information, and a test of given microscopic models. Although clearly $\theta_D(0)>0$ always, C may have either sign, depending on an average of $b_i(\theta,\varphi)$ over direction. In general, we expect that $b_i(\theta,\varphi)>0$, hence C as well, since the elastic wave velocities, $d\omega/dk$, must eventually decrease as k increases, and become zero near the Brillouin zone boundary [since $\omega(\mathbf{k})$ is a periodic function of $\mathbf{k}$]. However, the first deviations of the spectrum from the no-dispersion approximation could occur with the opposite sign and the elastic wave velocities could *increase* over a limited range of k. Then, particularly if such deviations occur in heavily weighted mode types and directions, $\theta_D(T)/\theta_D(0)$ might have an initial curvature upward. Such behavior has been suggested by Bhatia and Horton[2] for Pb on the basis of a particular force-constant model, and also by Horton and Schiff[5] for the three-constant, nearest-neighbor model, and we have verified the sign for the latter model, using (13) and evaluating the integral by highly accurate numerical methods (see Appendix II).

III. EQUIVALENT DEBYE THETA AT 0°K FOR CUBIC CRYSTALS

For cubic symmetry, the formula (12) for $\theta_D(0)$ simplifies to

$$\theta_D(0)=\theta_0' f(r_1,r_2), \tag{14}$$

where

$$\theta_0'=2.515\times10^{-3}c_{11}^{\frac{1}{2}}M^{-\frac{1}{3}}\rho^{-1/6} \text{ (cgs units)},$$

$$f(r_1,r_2)=\left[\frac{1}{12\pi}\int_{4\pi}\sum_{i=1}^{3}\frac{1}{v_{ri}^3}d\Omega\right]^{-\frac{1}{3}},$$

$$r_1=(c_{11}-c_{12})/2c_{11},$$

$$r_2=c_{44}/c_{11},$$

$$v_{ri}=v_i/v_0, \quad v_0=[c_{11}/\rho]^{\frac{1}{2}}.$$

Applying (14) to Ge, and using the computation procedures described briefly in Appendix II, and the elastic constants of McSkimin[13] gives $\theta_D(0)=374.0$°K. The explicit values of the five quantities whose numerical values determine $\theta_D(0)$ are[13]

$$c_{11}=1.3156\times10^{12} \text{ dynes/cm}^2 \text{ (at } -200\text{°C)},$$

$$c_{12}=0.4945\times10^{12} \text{ dynes/cm}^2 \text{ (at } -200\text{°C)},$$

$$c_{44}=0.6840\times10^{12} \text{ dynes/cm}^2 \text{ (at } -200\text{°C)}.$$

$$\rho=5.338 \text{ g/cm}^3 \text{ (at 0°K)}, \quad M=72.60.$$

The calculation is accurate to better than four figures.[14] The error in $\theta_D(0)$ is therefore due to errors in the five numerical constants and arises mainly from errors in the velocity measurements, which determine c_{11}, c_{12}, and c_{44}. Using the error of $\pm\frac{1}{2}\%$ in measured sound velocities quoted by McSkimin[13] leads to a possible error of $\pm\frac{1}{2}\%$ in $\theta_D(0)$, or about ±2°K.[15] (The error due to using elastic constants at -200°C instead of at 0°K is about -0.1%.)

This value of $\theta_D(0)$ may be compared with a value obtained from the specific heat measurements below 5°K of Keesom and Pearlman,[16] who estimate $\theta_D(0)=362\text{°K}\pm6\text{°K}$. This seems to be significantly lower than the value calculated above, and indicates either a systematic error, or a breakdown in the basic assumptions, such as the harmonic assumption or possibly the adiabatic assumption. The value of 362°K is based on an average of all specimens and data, and also on a fit involving a term linear in T, $C_v=aT+bT^3$. Without the linear term, the value of $\theta_D(0)$ would be even lower. Examination of the data for individual specimens shows considerable variation. Thus specimen SXII has $\theta_D(0)=368$°K and a downward curvature $(C>0)$, as expected, whereas specimen PXI has $\theta_D(0)=350$°K and an upward curvature $(C<0)$. These variations, the substantial discrepancy in $\theta_D(0)$ from the elastic and thermal measurements and the significance of this discrepancy, make it desirable to have more measurements on Ge in the helium-temperature region.[7]

IV. THE $\theta_D(T)$ CURVE FOR GE

Calculation of the specific heat at a finite temperature requires a knowledge of the complete frequency spectrum $\omega(\mathbf{k})$. Such knowledge could become available in

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[12] It is noteworthy, that if the assumptions which lead to (11) are known to hold accurately for some specimen, then (11) offers, in principle, a way of measuring the ratio of the two characteristic quantum constants, h and K, by macroscopic measurements. This is an aspect of the fact that at temperatures approaching 0°K, quantum effects are manifested on a macroscopic scale.

[13] H. J. McSkimin, J. Appl. Phys. **24**, 988 (1953).

[14] J. de Launay[6] with accurate integration procedures and the same constants also obtains 374.0°K (p. 300). We have developed a simple highly accurate procedure for evaluation of $f(r_1,r_2)$, and also prepared a chart of contour lines of constant $f(r_1,r_2)$. These procedures and results will be published separately; see P. Marcus and A. Kennedy, Bull. Am. Phys. Soc. Ser. II, **3**, 226 (1958).

[15] The error in $\theta_D(0)$ can be expressed in terms of errors in the elastic constants (ignoring errors in M and ρ) by

$$\frac{\Delta\theta_D(0)}{\theta_D(0)}=0.36\frac{\Delta c_{11}}{c_{11}}-0.12\frac{\Delta c_{12}}{c_{12}}+0.26\frac{\Delta c_{44}}{c_{44}},$$

which holds at the values for Ge. The errors in c_{11}, c_{12}, and c_{44} may then be easily expressed in terms of errors in the three particular measured velocities.

[16] P. H. Keesom and N. Pearlman, Phys. Rev. **91**, 1347 (1953).

a number of ways, illustrated by the following four possibilities:

(1) $\omega(\mathbf{k})$ could be measured directly by techniques like inelastic neutron scattering or diffuse x-ray scattering. As yet, however, only partial frequency spectra in a few special directions are available.

(2) The frequency spectrum could be calculated for a force-constant model, such as those used in Born's theory of lattice dynamics.[9] Such a model could, in principle, describe the dynamics of any lattice which satisfies the basic assumptions, provided enough force constants are used. In practice, however, only a limited number of force constants can be determined from known crystal properties, and force constants between high-order neighbors must therefore be assumed negligible. The resulting limited force-constant model serves as a parametric representation of the crystal properties, with the force constants as parameters or fitting constants. This representation thus has an arbitrary character, although it may rest on plausible physical arguments in particular cases, but does give rise to a definite specific heat curve which can be compared with measured curves. Good agreement between these curves is an indication of a possible reasonable model for the crystal, although such agreement does not establish the model.

A calculation of this kind has been made for Ge by Hsieh[17] using the Smith model for diamond-type lattices (2 nearest neighbor force constants and 1 next-nearest neighbor central force constant). The reduced $\theta_D(T)$ curve in Fig. 1 shows a considerable discrepancy from the available specific heat data of Hill and Parkinson, and Estermann and Weertman.[18] The deviations of this calculated $\theta_D(T)$ curve from the Debye approximation, for which $\theta_D(T)$ is a constant equal to $\theta_D(0)$, are much less than observed.

(3) A useful model may also be constructed by working directly with the frequency spectrum, hence avoiding the tedious step of calculating this from a force-constant model. A model of this kind, which uses all the elastic constants and the lattice structure in a plausible way to fix the frequency spectrum, is arrived at as follows. The initial downward curvature in $\theta_D(T)$ at $T=0$ arises from the dispersion of elastic waves, which lowers ω at given $\mathbf{k}$ (compared to the absence of dispersion), hence raises C_v at given T because the waves are more easily excited, and hence lowers $\theta_D(T)$. Now the dispersion in a one-dimensional lattice due to nearest-neighbor interaction is enough to produce changes in $\theta_D(T)$ of the same magnitude as in three dimensions.[19] Hence we can make a definite model with about the right amount of dispersion by assuming the simple dispersion formula of the one-dimensional chain holds in each direction, for each of the three acoustic mode types, namely

$$\omega_i(\mathbf{k})=v_i(\theta,\varphi)k\left(\sin\frac{\pi k}{2k_m(\theta,\varphi)}\right)\bigg/\frac{\pi k}{2k_m(\theta,\varphi)},\quad i=1,2,3. \tag{15}$$

The two parameters in (15), $v_i(\theta,\varphi)$ and $k_m(\theta,\varphi)$, are fixed by the acoustic wave velocity and the value of k at the Brillouin zone boundary in the direction θ, φ, respectively, thus using all the elastic and structural knowledge of the crystal. In addition (15) yields the correct value of $\theta_D(0)$, contains the correct total number of acoustical modes, and introduces a plausible amount of dispersion into the spectrum, so that it should be useful as a standard model whose specific heat may be compared with measurement. The nature of the deviations will then suggest the way in which the actual frequency spectrum deviates from the standard behavior (15), and modifications may be introduced.

Calculations of $\theta_D(T)$ based on this model, which will be called the simple dispersion model (S.D.M.), have been made for Ge and are also shown in Fig. 1. The curve is similar to Hsieh's curve, and is shallower than the experimental curve. Such a difference could arise from a greater dispersion in the actual spectrum than is assumed in the S.D.M. (or occurs generally in near-neighbor force-constant models) as will be shown later.[20]

(4) It is of considerable interest to make use of the recent data on the actual spectrum of Ge in certain directions, obtained with inelastic scattering of neutrons

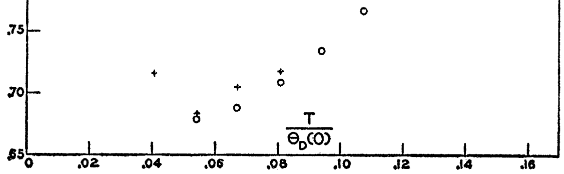

FIG. 1. The reduced equivalent Debye theta curve of Ge, $\theta_D(T)/\theta_D(0)$ *vs* $T/\theta_D(0)$ for the simple dispersion model, Hsieh's model, and the experimental data of Hill and Parkinson, Estermann and Weertman, and Keesom and Pearlman.

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[17] Y. Hsieh, J. Chem. Phys. **22**, 306 (1954).

[18] R. W. Hill and D. H. Parkinson, Phil. Mag. **43**, 309 (1952); I. Estermann and J. R. Weertman, J. Chem. Phys. **20**, 972 (1952).

[19] P. Marcus and A. Kennedy, Bull. Am. Phys. Soc. Ser. II, **1**, 142 (1956).

[20] It is of interest that the simple dispersion model applied to diamond (carbon) gives rather good agreement with recent measurements of D. L. Burk and S. Friedberg, Phys. Rev. **111**, 1275 (1958); these calculations will be published separately.

by Brockhouse and Iyengar,[21] since this shows that the transverse modes in the [111] and [100] directions have considerably more dispersion than the simple dispersion model assumes. The limited amount of direct information has been utilized in a calculation of $\theta_D(T)$ by assuming the $\omega(\mathbf{k})$ curve in any other direction is similar to that in the [111] or [100] direction, when expressed in reduced form. Namely, we assume

$$\frac{\omega(\mathbf{k})}{v_i(\theta,\varphi)k_m(\theta,\varphi)}=\frac{k}{k_m(\theta,\varphi)}+\sum_{n=1}^{4}a_n\left(\frac{k}{k_m(\theta,\varphi)}\right)^{2n+1},\quad i=2,3 \tag{16}$$

where a_n is independent of direction and $v_i(\theta,\varphi)$, $k_m(\theta,\varphi)$ are the same as in (15). Equation (16) refers to the two transverse modes, and the longitudinal modes are assumed given by (15) for simplicity. (We refer to this model as the modified dispersion model, M.D.M.) Since the transverse modes dominate, contributing 90% of the specific heat (see Appendix II), this assumption is not critical. The a_n are determined by fitting the observed [111] dispersion curves. (The [100] dispersion curve is similar, so for simplicity the [111] form is used throughout, see Fig. 3.) The nature of the fit is shown in Fig. 3 and discussed, with numerical values, in Appendix III.

The results of a specific heat calculation with this model are shown in Fig. 2; slightly different curves are given for the two sets of neutron data, which give an idea of the accuracy of determination of $\theta_D(T)$. There is a marked improvement in the agreement with the measurements. Particularly striking is the appearance now of about the right depth and position of the deep minimum; the calculated curves may, however, be slightly too low.[22]

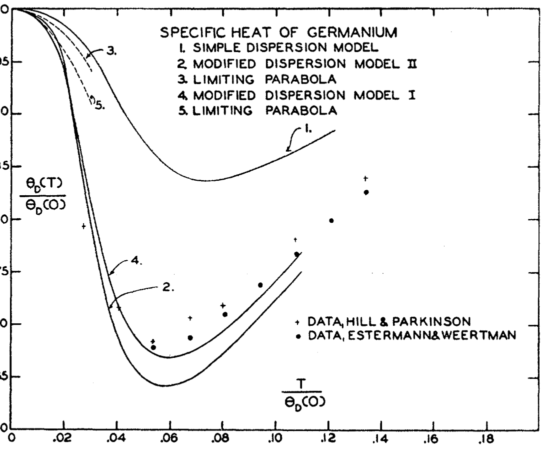

FIG. 2. The reduced equivalent Debye theta curve of Ge, $\theta_D(T)/\theta_D(0)$ *vs* $T/\theta_D(0)$ for the simple dispersion model, modified dispersion model I (based on data set I of Brockhouse and Iyengar, 1957), and modified dispersion model II (based on their data set II, 1958), and the experimental data of Fig. 1.

For each $\theta_D(T)$ curve in Fig. 2 the initial parabola was determined by a separate calculation using (13). This served to extrapolate the calculated curves accurately to 0°K. The measurements give no information on the curvature of this initial parabola, which is a good approximation at least to $T/\theta_D(0)=0.01$. The measurements below 5°K, as noted above, give no useful values, and additional measurements would be desirable. Numerical estimates of C are given in Appendix III, but the scatter of the neutron data leaves a considerable uncertainty in this quantity.

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APPENDIX I. EXPANSION OF THE FREQUENCY SPECTRUM IN POWERS OF k

The equations of motion of the lattice, under the assumptions of Sec. II, are satisfied by plane waves $\mathbf{u}_i e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}$, provided ω and k satisfy a secular equation. This equation is a polynomial in ω^2 (since only a second time derivative occurs in the equations of motion) with real coefficients which are analytic functions of $\mathbf{k}$, and the force constants. Now the wave with $-\mathbf{k}$ in place of $\mathbf{k}$ but the same ω is also a solution of the equations of motion (and the periodic boundary conditions), since complex conjugation and time reversal leave the equations of motion unchanged but change the sign of $\mathbf{k}$ in the plane wave solution. Thus the equation for ω^2 is the same for $-\mathbf{k}$ as for $+\mathbf{k}$ and the coefficients, A_n, of the various powers, ω^{2n}, of ω^2 must satisfy $A_n(\mathbf{k})=A_n(-\mathbf{k})$. This requires that in an expansion of A_n in powers of k_x, k_y, k_z, in any term the sum of the powers of k_x, k_y, k_z must be even. Hence in a fixed direction A_n is a function of k^2, the square of the magnitude of $\mathbf{k}$, or $A_n(k^2,\theta,\varphi)$. For the acoustic modes, ω^2 approaches k^2 as $k\rightarrow 0$, and since the coefficients of the polynomial equation for ω^2 depend only on k^2, any additional terms in the expansion of ω^2 in powers of k obtained from this equation can only bring in additional even powers.

APPENDIX II. CALCULATION PROCEDURES

We write Eq. (1) in the reduced form in terms of reduced variables as

$$\frac{C_v}{3NK}=\frac{1}{12}\int_{4\pi}d\Omega h(t,\varphi), \tag{17}$$

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[21] B. N. Brockhouse and P. K. Iyengar, Phys. Rev. **108**, 894 (1957) (data set I), and a more complete discussion in Phys. Rev. **111**, 747 (1958) (data set II). We are indebted to the authors for information in advance of publication.

[22] A test of this assumption is provided by measurements[21] of the frequency of one of the transverse modes at the Brillouin zone boundary. On the hexagonal face (for directions other than [111]), the values of ω given by (16) are lower than the measured values. This suggests that this model overestimates the dispersion of the transverse modes, hence overestimates the specific heat, and underestimates the values of $\theta_D(T)$, as is indicated in the comparison with the experimental data in Fig. 2.

where

$$h(t,\varphi)=\frac{k_m^3}{k_0^3}\int_0^1\sum_{i=1}^{3}\frac{e^{X_iy_i}}{(e^{X_iy_i}-1)^2}X_i^2y_i^2z^2dz, \tag{18}$$

and

$X_i=(\hbar/KT)v_ik_m$ (a dimensionless function of t, φ),

$y_i(z)=\omega_i(k)/v_ik_m$ (the reduced dispersion curve),

$z=k/k_m$,

$k_0^3=2\pi^3N/V$ $[=(2\pi/a)^3$ for the face-centered cubic lattice, cubic cell side $a]$.

For the simple dispersion model

$$y_i(z)=(2/\pi)\sin(\pi z/2);\quad i=1,2,3 \tag{19}$$

and for the modified dispersion model

$$y_i(z)=\sum_{n=1}^{5}a_nz^{2n+1};\quad i=2,3$$

but $y_1(z)=(2/\pi)\sin(\pi z/2)$ as in (19) (values of a_n for Ge are given in Appendix III). The limiting form of $h(t,\varphi)$, as $T\rightarrow 0$°K, is

$$h(t,\varphi)=\left(\frac{KT}{\hbar}\right)^3\frac{V}{N}\frac{2\pi}{15}\sum_{i=1}^{3}\frac{1}{v_i^3}. \tag{20}$$

The angular integration is based on the geometry of the Brillouin zone for the face-centered cubic lattice (the well-known 14-sided figure with 6 square faces and 8 hexagonal faces shown, for example, by Mott and Jones[23]) which provides a convenient means of incorporating the cubic symmetry. The minimum integration region consists of three triangular areas, $\frac{1}{8}$ of a square face and two regions each $\frac{1}{12}$ of a hexagonal face. In the coordinates $t(=\cos\theta)$, φ (where θ and φ are polar coordinates with respect to the axis through the face center), the integral is a simple double integral over a nearly rectangular area. The integral is done using high-efficiency Gaussian integration formulas (6 points in both t and φ coordinates) and gives an accuracy of more than six significant figures.

The calculation is greatly simplified by the fact that in each of these models the radial integrals (18) are functions of one parameter only, X_i. Thus, the process of evaluating them by numerical integration at the 108 points in the angular integration mesh, for various values of temperature, is avoided. This dependence on the parameter X has been approximated by suitable polynomials in $1/X$ or X for the different ranges of interest of $1/X$ ($1/X$ is near 0 for the low-temperature region). These approximations are accurate to better than four significant figures.

It is interesting to note the relative sizes of the various contributions to the heat capacity:

		0°K	$T/\theta_D(0)=0.06$
Transverse modes,	hexagonal face	75%	80%
	square face	15%	17%
Longitudinal modes,	hexagonal face	7%	2%
	square face	2%	1%

The major contribution is from the transverse modes, which have lower sound velocities, i.e., are more easily excited, than the longitudinal modes. The hexagonal-face contribution dominates that of the square face since, in addition to the fact that the hexagonal faces subtend a solid angle more than three times as great, they contain those directions near the [111] direction which have the lowest sound velocities.

A correction has been made to the calculated curves for the contribution to the specific heat due to the optical-mode vibration. This is assumed to be given by a single Einstein specific heat formula using the Raman frequency $\omega/2\pi=300$ cm^{-1}.[19] The plotted curves include this correction, which affects the value of $\theta_D(T)$ less than 0.005% for $T/\theta_D\leqslant 0.07$, and is 0.14% at $T/\theta_D=0.10$.

APPENDIX III. FITTING FORMULAS FOR MEASURED DISPERSION CURVES

The dispersion curves for the transverse modes are based on the measured curve in the [111] direction.

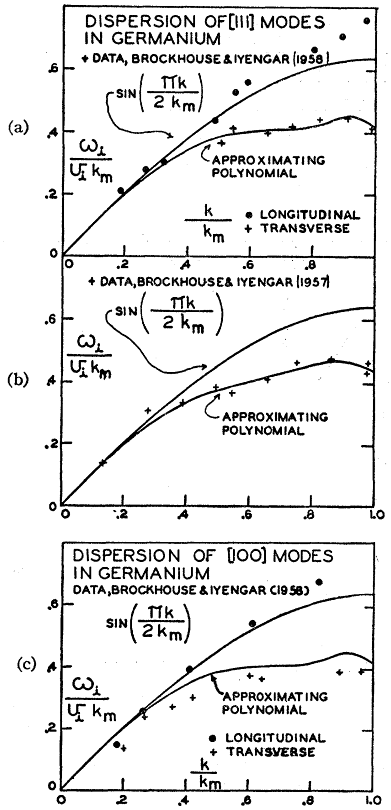

FIG. 3. The measured reduced dispersion curves ω_i/v_ik_m vs k/k_m for Ge with approximating polynomials: (a) [111] direction, based on data set II of Brockhouse and Iyengar, 1958; (b) [111] direction, their data set I, 1957; and (c) [100] direction, their data set II, 1958.

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[23] N. F. Mott and H. Jones, *Properties of Metals and Alloys* (Oxford University Press, Oxford, 1936), p. 70.

TABLE I. Data of Brockhouse and Iyengar.[a]

	1957 Data set I	1958 Data set II
a_1	-1.091	-0.687
a_2	$+0.110$	-2.002
a_3	$+1.691$	$+4.594$
a_4	-1.283	-2.489

[a] See reference 21.

The dispersion curve in any direction is assumed to be of the same form, in reduced k, as in the [111] direction, with the initial slope determined by the sound velocity.[22] Thus

$$\frac{\omega_i}{v_i k_m}=\frac{k}{k_m}+\sum_{n=1}^{4} a_n\left(\frac{k}{k_m}\right)^{2n+1}, \qquad i=2,3. \qquad (16)$$

The a_n, for the two sets of neutron spectrometry data, are given in Table I. Figures 3(a) and (b) show the data and the fitting polynomial; Fig. 3(c) shows the measured data in the [100] direction with the assumed dispersion curve. The a_n were fixed by least-squares fitting of all the data.

The longitudinal modes are approximated by the dispersion curve of the S.D.M.; a comparison with the neutron spectrometry data is shown in Figs. 3(a) and (c).

The coefficient C, fixing the limiting curvature of the reduced $\theta_D(T)$ curve [see Eq. (13)] is determined for these models by the coefficient a_1. Values for this curvature coefficient C are 98 for M.D.M. I, 62 for M.D.M. II, and 38 for S.D.M.

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Deduction of the Volume Dependence of the Cohesive Energy of Solids from Shock-Wave Compression Measurements*

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By applying the Mie-Grüneisen equation of state to measurements of the compression of solids by strong shock waves, it is possible to determine the volume dependence of the cohesive energy. The method for carrying out this deduction is presented along with a detailed exposition of the underlying assumptions. The method is applied to six metals Be, Al, Co, Ni, Cu, and Ag for which the experimental data are most extensive. The volume dependence of the cohesive energy for these six metals is presented in both analytical and graphical form.

I. INTRODUCTION

THE cohesive energy of a crystalline solid is the energy release upon assembling the constituent atoms from infinity to form the ordered array characteristic of that crystal. This energy is of fundamental significance in the theory of solids because it is a measure of the detailed nature of the spatial distribution of charge throughout the solid. The dependence of the cohesive energy Φ on the size of the atomic polyhedron is the most important factor which determines the lattice constant and the compressibility of the solid. Because of the crucial role of the cohesive energy in determining the density of the solid it is possible to deduce the volume dependence of Φ from measurements of the volume compression under pressure. The timeliness of such a deduction arises out of recent advances in the theory of cohesion,[1,2] and in the experimental methods for high-pressure compression of solids.[3,4]

The new theoretical advances[5] consist in the application of the "quantum defect" method[1] to the calculation of the volume dependence of the cohesive energy for multivalent metals with nonoverlapping cores.

The new experiments make use of strong shock waves to generate pressures which are typically in the 150 000- to 500 000-atmos region, but can be as large as 1 300 000 atmos. Under such stresses the volume compression of the solid is typically as large as 20%, but it can be as large as 40%.

The present paper applies the Mie-Grüneisen equation of state to the shock-wave data obtained by the Los Alamos group,[3] to deduce the volume dependence of Φ. A general procedure for this deduction

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† A large portion of this work was carried out while the author was a Summer Staff Member of the Los Alamos Scientific Laboratory, Los Alamos, New Mexico.

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[2] H. Brooks, Suppl. Nuovo cimento **7**, 165 (1958).

[3] Walsh, Rice, McQueen, and Yarger, Phys. Rev. **108**, 196 (1957).

[4] Rice, McQueen, and Walsh in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 6.

[5] H. Brooks (private communication).