

wave vectors about half way to the zone edge depart seriously from Bloch waves and the Fermi surface would appear to be a concept of limited utility in this region. Besides, the experimental data used by Moss is of uncertain accuracy near the region of interest. We find the $N_{1'}-N_1$ gap to be 2.2 eV, whereas the value due to Amar, Johnson, and Wang for this gap is 1.5 eV. Thus, our calculation gives a Fermi surface for which the departure from sphericity is greater than that given by the virtual-crystal approximation. In order to carry this comparison further we have calculated the $N_{1'}-N_1$ gap following the method presented in this paper but using atomic potentials for copper and zinc. These were the potentials used by Amar, Johnson, and Wang² in their VCA calculation. Our calculation gives a value 2.4 eV for the $N_{1'}-N_1$ gap. Thus the energy gap for the disordered alloy also is sensitive to the choice of potential,

but it is clear that striking difference in the values of $N_{1'}-N_1$ gap given by the present method and by the VCA approach originates from the differences in the formalisms. The virtual-crystal approximation is an over simplification of the alloy problem and the present approach may be regarded as an improvement in the sense that it recognizes the distinction between the constituents, takes account of the short-range order, and incorporates the lifetime effects for the electronic states.

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Critique of Current Theories of Akhieser Damping in Solids

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There are two widely used theories of ultrasonic attenuation in the Akhieser ($\Omega\tau \ll 1$) regime. Woodruff and Ehrenreich used the Boltzmann equation and found that the attenuation was a function of the specific heat of the thermal phonons. Mason and Bateman obtained the fundamentally different result that the attenuation also involved the thermal energy. It is shown here that the Mason-Bateman theory contains both mathematical and conceptual errors and that its apparent agreement with experimental data on Si and Ge is fortuitous.

I. INTRODUCTION

ULTRASONIC attenuation in dielectric single crystals is usually dominated by interaction of the ultrasonic wave with thermal phonons. If $\Omega\tau < 1$ (where Ω is the radian frequency of the ultrasonic wave and τ is a typical thermal-phonon relaxation time), the attenuation occurs via a mechanism first described by Akhieser.¹ Because of the anharmonicity of the medium, the strain produced by the sound wave modulates the frequencies of the thermal-phonon modes. The equilibrium populations of these modes are therefore modulated also. However, the *actual* populations, since they require a time τ to readjust to the new equilibrium conditions, lag in phase behind the driving sound wave. The reestablishment of equilibrium is an entropy-producing process with a consequent absorption of energy from the sound wave.

There have been a number of theoretical treatments of Akhieser damping.¹⁻⁸ The most thorough is the work

of Woodruff and Ehrenreich² who obtain an expression for the attenuation A (on a Debye model with $\Omega\tau \ll 1$) in the form

$$A = \beta C_V T \gamma_{av}^2 \Omega^2 \tau / 3\rho v^3 \quad (\text{nepers/unit length}), \quad (1)$$

where C_V is the specific heat per unit volume, T is the absolute temperature, γ_{av} is some average Grüneisen constant, ρ is the mass density, v is the ultrasonic velocity, and β is a numerical factor of order unity which depends on the form assumed for the local equilibrium distribution of thermal phonons.² The precise value of β is usually not important since γ_{av} is usually treated as an adjustable parameter.

A different result was obtained by Mason and Bateman,⁷ who made the important contribution of considering the anisotropy of the Grüneisen tensor as

¹ P. G. Klemens, in *Physical Acoustics*, edited by W. P. Mason (Academic Press Inc., New York, 1965), Vol. III B, pp. 228-232.

² S. Simons, Proc. Phys. Soc. (London) **83**, 749 (1964).

⁶ E. Prohovsky, IEEE Trans. Sonics Ultrasonics **SU-14**, 109 (1967).

⁷ W. P. Mason and T. B. Bateman, J. Acoust. Soc. Am. **36**, 644 (1964). See also W. P. Mason in Ref. 4, Vol. III B, pp. 256-267.

⁸ H. J. Maris, Phys. Rev. **175**, 1077 (1968).

¹ A. Akhieser, J. Phys. (U.S.S.R.) **1**, 277 (1939).

² T. O. Woodruff and H. Ehrenreich, Phys. Rev. **123**, 1533 (1961).

³ H. E. Bommel and K. Dransfeld, Phys. Rev. **117**, 1245 (1960).

determined from third-order elastic constant measurements. They found the attenuation of a longitudinal strain wave S_1 to be given by

$$A = \frac{1}{2\rho v^3} \left\{ 3 \sum_i E(i) [\gamma_1(i)]^2 - \gamma_i^2 C_V T \right\} \frac{\Omega^2 \tau}{1 + \Omega^2 \tau^2}, \quad (2)$$

where the thermal phonons have been divided into angular sectors and polarization branches, collectively denoted by the index i . $E(i)$ is the energy per unit volume of the i th group of thermal phonons and $\gamma_1(i)$ is their Grüneisen constant. γ_i is the average Grüneisen constant determined from the thermal expansion. Equation (2) is fundamentally different from Eq. (1) since it involves the thermal energies $E(i)$ rather than $C(i)T$ [where $C(i)$ is the specific heat of the i th group] and therefore gives a different temperature dependence for the attenuation. Equation (2) gave a good fit to Mason and Bateman's data on silicon and germanium, although they found it necessary to adjust τ somewhat. It is the purpose of this paper to suggest that this agreement was fortuitous and that Mason and Bateman's derivation is incorrect.

A brief summary of Woodruff and Ehrenreich's derivation, incorporating the same simplifying assumptions as used by Mason and Bateman, is presented in the next section. One important result derived there is that the attenuation should be zero for the (clearly unphysical) case where all phonon modes have the same Grüneisen constant, i.e., $\gamma_1(i) = \gamma$ for all i , provided the thermal-phonon distribution is spatially homogeneous so that there is no thermoelastic loss. Equation (2) obviously does not satisfy this condition.

Section III reviews the Mason-Bateman work and points out some errors both in the algebraic manipulations involved and in the conceptual basis of their derivation. Section IV discusses the application of both of these theories to experimental data.

II. WOODRUFF-EHRENREICH THEORY

The Woodruff-Ehrenreich theory is a very general treatment of Akhieser damping based on the Boltzmann equation. In fact, the results are too complete to be applied directly to experimental data and simplifications are inevitably required. In this section, the Woodruff-Ehrenreich derivation is repeated, employing the simplifying assumptions at the outset rather than specializing a general result at the end. In this manner the basic elements of the theory can be seen more clearly, and comparison with Mason and Bateman is facilitated.

Consider a strain wave S propagating along the x axis,

$$S \propto e^{i(Kx - \Omega t)}, \quad (3)$$

where K is the magnitude of the wave vector, Ω is the (radian) frequency, and the real part of all complex

quantities is implied. This strain wave modulates the frequency $\omega(\mathbf{k}\mu)$ of the thermal-phonon mode of wave vector \mathbf{k} and branch index μ according to the relation

$$\begin{aligned} \omega(\mathbf{k}\mu) &= \omega_0(\mathbf{k}\mu) [1 - \gamma(\mathbf{k}\mu)S + \dots] \\ &\equiv \omega_0(\mathbf{k}\mu) + \Delta\omega(\mathbf{k}\mu) + \dots, \end{aligned} \quad (4)$$

where $\gamma(\mathbf{k}\mu)$ is a generalized Grüneisen constant which depends on the propagation direction and polarization of S . The subscript zero denotes the value of a quantity in the absence of strain. For small strains, the higher-order terms in Eq. (4) will not contribute to the attenuation.

Because of this modulation, the instantaneous population of the mode $n(\mathbf{k}\mu)$ differs from its thermal equilibrium value $N_0(\omega_0(\mathbf{k}\mu))$ by an amount $\Delta n(\mathbf{k}\mu)$; i.e.,

$$n(\mathbf{k}\mu) = N_0(\omega_0(\mathbf{k}\mu)) + \Delta n(\mathbf{k}\mu), \quad (5)$$

where

$$N_0(\omega) = (e^{\hbar\omega/k_B T} - 1)^{-1}, \quad (6)$$

k_B being Boltzmann's constant.

The populations $n(\mathbf{k}\mu)$ are determined, in general, by solving the linearized Boltzmann equation. However, a great simplification results by neglecting the spatial terms in the Boltzmann equation or, equivalently, assuming the x component of the thermal-phonon group velocity to be zero. Then the Boltzmann equation becomes simply

$$\left. \frac{\partial n(\mathbf{k}\mu)}{\partial t} \right|_{\text{coll}} = \frac{\partial \Delta n(\mathbf{k}\mu)}{\partial t}. \quad (7)$$

This assumption was, in effect, also employed by Mason and Bateman. Although at first it appears rather drastic, Woodruff and Ehrenreich have shown that it does not have much effect on their results if $\Omega\tau \ll 1$. It does, however, become very important if $\Omega\tau > 1$.

The physics in the problem lies in the construction of an approximation to the collision term in Eq. (7). Woodruff and Ehrenreich discussed a form of the relaxation time approximation, based on the Callaway theory of thermal conductivity, which distinguished between normal and umklapp phonon collision processes. Maris⁸ generalized this approach further by including a relaxation term describing elastic collisions of phonons with impurities. However, the available experimental data, and its analysis, is never sufficiently detailed to permit an accurate determination of separate normal, umklapp, and impurity relaxation times and their dependence on \mathbf{k} , μ , and temperature.⁹ Again simplification is necessary.

The basic features of Akhieser damping may be obtained by assuming that $n(\mathbf{k}\mu)$ decays towards a Bose-Einstein distribution characterized by the instantaneous local frequency $\omega(\mathbf{k}\mu)$ and a modulated local temperature $T'(\mathbf{r}, t)$ which is to be determined self-consistently.

⁹ M. G. Holland, Phys. Rev. **132**, 2461 (1963).

In other words,

$$\left. \frac{\partial n(\mathbf{k}\mu)}{\partial t} \right|_{\text{coll}} = - \frac{n(\mathbf{k}\mu) - N_0'(\omega(\mathbf{k}\mu))}{\tau(\mathbf{k}\mu)}, \quad (8)$$

where

$$N_0'(\omega) = (e^{\hbar\omega/k_B T'} - 1)^{-1}. \quad (9)$$

In practice $\tau(\mathbf{k}\mu)$ will frequently be taken to be the same for all modes.

The physical significance of T' has been discussed somewhat by Woodruff and Ehrenreich. It may be regarded as a phenomenological expression of the fact that mode $(\mathbf{k}\mu)$ is not only losing population by scattering into other modes, but is also gaining population because of the decay of other modes. The totally local character of this approximation is consistent with our neglect of thermal-phonon group velocities.

Since $\Delta\omega(\mathbf{k}\mu)$ is small for a small amplitude sound wave, N_0' may be expanded in a Taylor series, and Eq. (8) becomes

$$\left. \frac{\partial n}{\partial t} \right|_{\text{coll}} \approx - \left[\left(\frac{\partial N_0'(\omega)}{\partial \omega} \right)_0 \Delta\omega + \left(\frac{\partial N_0'(\omega)}{\partial T'} \right)_0 \Delta T - \Delta n \right], \quad (10)$$

where

$$\Delta T = T'(\mathbf{r}, t) - T. \quad (11)$$

The $(\mathbf{k}\mu)$ indices have been dropped, and the subscript zero on the derivatives means that they are to be evaluated at $\Delta T = 0$ and $\Delta\omega = 0$.

Equation (7) may now be solved formally by assuming plane-wave solutions,

$$\Delta T, \Delta\omega, \Delta n \sim \exp i[Kx - \Omega t]. \quad (12)$$

The result is

$$\Delta n = \omega_0 \left(\frac{\partial N_0'}{\partial \omega} \right)_0 \left(\frac{\Delta\omega}{\omega_0} - \frac{\Delta T}{T} \right) / (1 - i\Omega\tau). \quad (13)$$

In deriving this result, we have made use of the fact that N_0' is a function only of ω/T' , so that

$$\omega_0 \left[\frac{\partial N_0'}{\partial \omega} \right]_0 = -T \left[\frac{\partial N_0'}{\partial T} \right]_0 = - \frac{TC(\mathbf{k}\mu)}{\hbar\omega_0}, \quad (14)$$

where $C(\mathbf{k}\mu)$ is the contribution of mode $(\mathbf{k}\mu)$ to the specific heat at constant volume if we ignore the temperature dependence of $\omega_0(\mathbf{k}\mu)$.

The temperature shift ΔT may be determined by the condition that all collision processes conserve energy to *first order in the strain*. Irreversibility occurs only in second order, since the irreversible energy loss must be proportional to the energy in the strain wave, which of course is quadratic in strain. Therefore,

$$\sum_{\mathbf{k}\mu} \hbar\omega_0(\mathbf{k}\mu) \left(\frac{\partial n(\mathbf{k}\mu)}{\partial t} \right)_{\text{coll}} = 0. \quad (15)$$

Note that the unperturbed frequency ω_0 appears here. A more rigorous derivation of Eq. (15) was given by Akhieser.¹ Substituting from Eqs. (10) and (14), we obtain

$$\sum_{\mathbf{k}\mu} \left[\frac{CT}{\tau} \left(\frac{\Delta\omega}{\omega_0} - \frac{\Delta T}{T} \right) + \frac{\hbar\omega_0 \Delta n}{\tau} \right] = 0. \quad (16)$$

Combining Eqs. (13) and (14) gives

$$\hbar\omega_0 \Delta n = -CT \left(\frac{\Delta\omega}{\omega_0} - \frac{\Delta T}{T} \right) (1 - i\Omega\tau)^{-1}. \quad (17)$$

Substituting Δn from Eq. (17) into Eq. (16) yields

$$\sum \left\{ CT \left(\frac{\Delta\omega}{\omega_0} - \frac{\Delta T}{T} \right) \left[\frac{1}{1 - i\Omega\tau} \right] \right\} = 0, \quad (18)$$

and therefore,

$$\frac{\Delta T}{T} = \sum CT \frac{\Delta\omega}{\omega_0} (1 - i\Omega\tau)^{-1} / \sum CT (1 - i\Omega\tau)^{-1}. \quad (19)$$

Here C , $\Delta\omega/\omega_0$, τ , and Δn can, in general, all depend on \mathbf{k} and μ .

In principle, ΔT may be eliminated from Eq. (17) in order to obtain Δn for every mode, and the attenuation is then given by⁸

$$A = \frac{\hbar\Omega}{2\rho v^3 V} \sum_{\mathbf{k}\mu} \gamma \omega_0 \text{Im} \frac{\Delta n}{S}, \quad (20)$$

where V is the crystal volume.

Now, if $\Delta\omega/\omega_0$ is independent of \mathbf{k} and μ , that is, all modes have the same Grüneisen constant, it is easy to show that the attenuation is zero (provided spatial terms in the Boltzmann equation are neglected). From Eq. (19), if $\Delta\omega/\omega_0$ may be removed from the sum,

$$\Delta T/T = \Delta\omega/\omega_0, \quad (21)$$

and it follows from Eqs. (17) and (20) that $\Delta n = 0$ and $A = 0$.

Woodruff and Ehrenreich obtained the result, for a simple Debye model with all $\Delta\omega/\omega$ (their a) equal, that

$$\Delta T/T = (\Delta\omega/\omega) I_{00}/I_{01}, \quad (22)$$

where I_{00} and I_{01} are angular integrals. This led to a nonvanishing Δn and, in fact, simply introduced a factor of $\frac{2}{3}$ in the attenuation (for $\Omega\tau \ll 1$) when compared to the case of ignoring ΔT altogether. However, the difference between I_{00} and I_{01} may be traced to spatial derivatives in the Boltzmann equation. If the group velocity c_z is set equal to zero in Woodruff and Ehrenreich's Eq. (2.24), then the $\Delta T/T$ term and the $\Delta\omega/\omega$ terms both involve I_{00} , and Eq. (21) is again obtained for all $\Delta\omega/\omega$ equal.

The physical interpretation of Eq. (22) is that the system is not quite adiabatic even if $\Omega\tau \ll 1$. There is still some heat flow which tends to reduce $\Delta T/T$. For this simple model in the $\Omega\tau \ll 1$ limit, Eq. (22) can be shown to reduce to

$$\Delta T/T = (1 - \frac{1}{3}i\Omega\tau)\Delta\omega/\omega. \quad (23)$$

However, one can "turn off" this effect, which is just the classical thermoelastic loss,⁸ by setting the group velocity, and hence the thermal conductivity, to zero. Then truly adiabatic conditions prevail, and the damping must vanish if all modes have the same Grüneisen constant.

III. MASON-BATEMAN THEORY

A. Review of Derivation

The Mason-Bateman theory is based on the equation

$$A = (\Delta c/2\rho v^3)\Omega^2\tau/(1 + \Omega^2\tau^2), \quad (24)$$

where

$$\Delta c = c_\infty - c_0, \quad (25)$$

and c_∞ and c_0 are the appropriate dynamic elastic moduli at infinite frequency and zero frequency, respectively. A succinct derivation of Eq. (24) has been given by Prohofsky.⁸ This derivation was for a spatially homogeneous model. It therefore includes only Akhiezer damping and not thermoelastic losses.

Mason and Bateman calculate Δc from the thermal-phonon contribution to the internal energy,

$$U_{\text{th}} = \sum_{\mathbf{k}\mu} [n(\mathbf{k}\mu) + \frac{1}{2}] \hbar\omega(\mathbf{k}\mu). \quad (26)$$

For a high-frequency (or suddenly applied) strain, the stress σ is given by¹⁰

$$\sigma_\infty = \left. \frac{\partial U_{\text{th}}}{\partial S} \right|_{n(\mathbf{k}\mu)} + c^*S \equiv c_\infty S, \quad (27)$$

where c^*S is the strain derivative of the mechanical potential energy.

Mason and Bateman use a Debye model to express the sum in Eq. (26), excluding the zero-point energy, as an integral involving a density-of-states function,

$$U_{\text{th}} = 3\hbar \sum_i \frac{N_i}{\omega_{gi}^3} \int_0^{\omega_{gi}} \frac{\omega^3 d\omega}{[\exp(\hbar\omega/k_B T) - 1]}, \quad (28)$$

where N_i is the number of phonons in the i th group and ω_{gi} is the corresponding limiting frequency (the Debye frequency). ω_{gi} has a dependence on strain analogous to that given by Eq. (4) for a general $\omega(\mathbf{k}\mu)$. All modes in the i th group are assumed to have the same Grüneisen constant $\gamma(i)$.

In carrying out the differentiation indicated in Eq. (27), Mason and Bateman argue that the integral

¹⁰H. J. Maris, *Phil. Mag.* 16, 331 (1967).

in Eq. (28) is independent of strain. They therefore obtain

$$\begin{aligned} \sigma_\infty &= c^*S - 9\hbar \sum_i \frac{N_i}{\omega_{gi}^3} \left\{ \frac{\partial \omega_{gi}/\partial S}{\omega_{gi}} \right\} \int_0^{\omega_{gi}} \frac{\omega^3 d\omega}{\exp(\hbar\omega/k_B T) - 1} \\ &= c^*S - 3 \sum_i E(i) \left\{ \frac{\partial \omega_{gi}/\partial S}{\omega_{gi}} \right\}. \end{aligned} \quad (29)$$

From Eq. (4),

$$\sigma_\infty = c^*S + 3 \sum_i \frac{E(i)\gamma(i)}{1 - \gamma(i)S} \quad (30)$$

and for small $\gamma(i)S$,

$$\sigma_\infty \approx c^*S + 3 \sum_i E(i)[\gamma(i)]^2 S + 3 \sum_i E(i)\gamma(i). \quad (31)$$

The coefficient of S in this equation is identified as c_∞ .

It is then argued that c_0 is given by

$$c_0 = c^* + \gamma_i^2 \rho C_v T, \quad (32)$$

and Eq. (2) follows by substituting Eq. (32) and c_∞ from Eq. (30) into Eq. (24).

B. Discussion of Mathematical Manipulations

A number of steps in the above derivation are contestable on purely analytical grounds. The first questionable step is in the transition from Eq. (29) to Eq. (30). Note that $E(i)$ in Eq. (30) was treated as the thermal energy in the absence of strain; the contribution to c_∞ from the strain dependence of $E(i)$ was not considered. The factor ω_{gi}^{-4} in Eq. (29), which came from $\partial(\omega_{gi}^{-3})/\partial S$, was arbitrarily split into $\omega_{gi}^{-3}\omega_{gi}^{-1}$. The ω_{gi}^{-3} part was incorporated into $E(i)$ and treated as strain-independent. The ω_{gi}^{-1} part, however, was treated as an explicit function of strain. Therefore the denominator in the summand of Eq. (30) should properly be $[1 - \gamma(i)S]^4$ instead of $[1 - \gamma(i)S]$ if $E(i)$ in the numerator is to be treated as strain-independent. Then, since

$$[1 - \gamma(i)S]^{-4} \approx 1 + 4\gamma(i)S, \quad (33)$$

an additional factor of 4 should appear in the second term on Eq. (31).

More important, the assertion that the integral in Eq. (28) is independent of strain is valid only if $\hbar\omega_{gi}/k_B T \gg 1$ in which case the upper limit may be replaced by infinity. This is just the circumstance under which the specific heat varies as T^3 . Thus, the treatment is not valid above the T^3 region, a severe restriction. Mason and Bateman argue that the integral is invariant under strain because it is summing the same number of frequencies at the same occupation numbers when ω_{gi} is changed by the strain. This argument is incorrect, since the total number of states depends both on the density of states ($\propto \omega^2/\omega_{gi}^3$) and on the cutoff frequency ω_{gi} in the upper limit of integration. Varying one quantity and not the other does not leave the total number of states

constant. If attention is restricted to the $C_v \sim T^3$ region, then

$$C(i)T = 4E(i), \quad (34)$$

where $C(i)$ is the specific heat of the i th group. In other words, the Mason-Bateman result in this regime does, in fact, involve $C(i)T$ rather than $E(i)$, although the distinction is only a numerical factor.

The Mason-Bateman prescription can also be carried through at higher temperatures, where the distinction between $C(i)T$ and $E(i)$ is more important. If the upper limit of integration is differentiated properly, and all linear strain dependences in σ_∞ are retained, then again $C(i)$ appears consistently rather than $E(i)$. These results will not be presented here because we believe the entire procedure to be conceptually unsound as discussed in the next section.

C. Conceptual Basis

The essential elements of the Mason-Bateman derivation are more evident if the Debye model is dispensed with. Using the more general expression for U_{th} , Eq. (26), rather than the integral form, Eq. (28), the expression for σ_∞ becomes

$$\begin{aligned} \sigma_\infty &= c^s S + \left. \frac{\partial U_{\text{th}}}{\partial S} \right|_{n(\mathbf{k}\mu)} \\ &= c^s S + \sum_{\mathbf{k}\mu} \left[n(\mathbf{k}\mu) + \frac{1}{2} \right] \hbar \frac{\partial \omega(\mathbf{k}\mu)}{\partial S} \\ &= c^s S - \sum_{\mathbf{k}\mu} \left[n(\mathbf{k}\mu) + \frac{1}{2} \right] \hbar \omega_0(\mathbf{k}\mu) \gamma(\mathbf{k}\mu). \end{aligned} \quad (35)$$

At this point we can proceed on one of three assumptions: (a) $n(\mathbf{k}\mu)$ can be treated as the *unstrained* equilibrium value $N_0(\omega_0(\mathbf{k}\mu))$; (b) $n(\mathbf{k}\mu)$ can be treated as the *actual* instantaneous population as determined by the Boltzmann equation; or (c) $n(\mathbf{k}\mu)$ can be treated as the *instantaneous equilibrium* value $N_0(\omega(\mathbf{k}\mu))$. It will be shown that the first two assumptions are equivalent in the present case and both lead to $c_\infty \equiv c^s$. The third assumption, which was, in effect, the assumption used by Mason and Bateman, leads to a negative attenuation.

(a) It is immediately evident that replacing $n(\mathbf{k}\mu)$ by $N_0(\omega_0(\mathbf{k}\mu))$ leads to $c_\infty \equiv c^s$, since $N_0(\omega_0(\mathbf{k}\mu))$ is independent of strain. The only remaining strain-dependent term in σ_∞ is $c^s S$. Strain-independent terms in the stress may simply be lumped into the definition of the stress-free state. In other words the thermal-phonon part of c_∞ makes no contribution to the attenuation.

(b) This same result is obtained using $n(\mathbf{k}\mu)$ derived from the Boltzmann equation (disregarding the spatial terms). Remembering Eq. (15), the definition of c_∞ , and using Eq. (13), then as $\Omega\tau \rightarrow \infty$, $\Delta n \rightarrow 0$, and $n(\mathbf{k}\mu) \rightarrow N_0(\omega_0(\mathbf{k}\mu))$. This result can also be obtained from the more detailed analysis carried out by Maris¹⁰

by setting the group velocity equal to zero in the last term of his Eq. (21). (The other terms in that equation come from anharmonic effects which are not considered here but which do not contribute to the attenuation, since they appear in both c_0 and c_∞ .)

(c) Although the results obtained above indicate that there is no thermal-phonon contribution to c_∞ in a spatially homogeneous system, the one remaining assumption, $n(\mathbf{k}\mu) = N_0(\omega(\mathbf{k}\mu))$, can be tried in order to force a nonvanishing contribution. By expanding $N_0(\omega(\mathbf{k}\mu))$ in a Taylor series as in Eq. (10), Eq. (35) becomes

$$\begin{aligned} \sigma_\infty &= c^s S - \sum N_0(\omega) \omega_0 \gamma \\ &= c^s S - \sum N_0(\omega_0) \omega_0 \gamma - \sum \omega_0 \gamma \left. \frac{\partial N_0}{\partial \omega} \right|_0 \Delta \omega \\ &= c^s S - \sum N_0(\omega_0) \omega_0 \gamma + \sum \omega_0^2 \gamma^2 S \left. \frac{\partial N_0}{\partial \omega} \right|_0, \end{aligned} \quad (36)$$

where we have dropped the zero-point term and the $(\mathbf{k}\mu)$ indices. The last term in this equation is now linear in S and therefore contributes to c_∞ . By utilizing Eq. (14), we may write

$$c_\infty = c^s - \sum (\gamma(\mathbf{k}\mu))^2 C(\mathbf{k}\mu) T. \quad (37)$$

Although this term has the correct form, involving $C(\mathbf{k}\mu)T$, it has the incorrect sign. Therefore, the only route which we can take from Eq. (35) and get a non-zero effect leads to a negative attenuation [see Eqs. (24) and (25)]. This third assumption is actually correct for calculating c_0 rather than c_∞ , although it is difficult to justify rigorously.¹⁰ Then the sign is easy to understand, since a negative contribution to c_0 is a positive contribution to the attenuation.

We are therefore led to the conclusion that the entire thermal-phonon contribution to A must be contained in c_0 for a spatially homogeneous system. [See also the last term of Eq. (28) in Ref. 10.] For a real spatially inhomogeneous system, of course, this conclusion no longer holds. The Landau-Rumer results,¹¹ or the Woodruff and Ehrenreich result with spatial terms retained, both give a finite dissipation in the limit $\Omega\tau \rightarrow \infty$, whereas Eq. (24) does not. It can also be shown^{8,10} that with a correct calculation of Δc , Eq. (24) does, in fact, give the Woodruff-Ehrenreich results.

IV. COMPARISON WITH EXPERIMENT

Mason and Bateman's work also presents measurements of the ultrasonic attenuation on samples of Ge and Si. Both longitudinal and shear wave attenuation was measured and the data were taken between room temperature and liquid-He temperature at several fixed frequencies between 286 and 495 MHz. The longitudinal

¹¹ L. Landau and G. Rumer, *Physik Z. Sowjetunion* 11, 18 (1937).

wave results were compared both to their theory, Eq. (2), and to a theory due to Bommel and Dransfeld.³ Bommel and Dransfeld's result is, basically, Eq. (1) with $\Omega^2\tau$ replaced by $\Omega^2\tau/(1+\Omega^2\tau^2)$.¹²

The simple kinetic theory expression for thermal conductivity κ ,

$$\kappa = \frac{1}{3}C_V v_D^2 \tau_{th}, \quad (38)$$

was used to obtain τ_{th} . Here v_D is the Debye velocity. The derived value of τ_{th} was used in the Bommel-Dransfeld equation and an average γ was used to obtain agreement at room temperature. The assumption that $\tau = 2\tau_{th}$ for longitudinal waves was used in the Mason-Bateman theory, and the Grüneisen constants were calculated from third-order elastic constant data.

The agreement between theory and experiment is very good for the Mason-Bateman theory but poor for the Bommel-Dransfeld equation. The disagreement with Bommel-Dransfeld is most severe near 50°K for Ge and 100°K for Si. The data on shear-wave attenuation were compared only with the Mason-Bateman theory, using $\tau = \tau_{th}$, and the agreement is within about 50% over the entire range. This section will try to indicate the reasons for the poor agreement of the Bommel-Dransfeld (or Woodruff-Ehrenreich) equation in the region 50 to 100°K and also show where Mason and Bateman's assumptions are invalid.

It is well known that Si and Ge each have a very dispersive transverse acoustic (TA) phonon branch.^{13,14} In Si, for example, the zone boundary intercept of this TA branch in the [100] direction is at $\hbar\omega/k_B = 190^\circ\text{K}$, whereas the extrapolated (dispersionless) intercept is at 430°K. This strong dispersion makes it very difficult to determine the individual $E(i)$ in Eq. (2). Mason and Bateman simply assume that all the $E(i)$ are the same, which is a particularly severe approximation at low temperature, since there $E(i) \sim \omega_{\theta i}^{-3}$. The TA modes should therefore be weighted more heavily than the longitudinal acoustic (LA) modes. At very high temperatures, such that $\hbar\omega_{\theta i} \ll kT$, $E(i) \rightarrow 3N_i/k_B T$, and setting all $E(i)$ equal is more reasonable. However, at the temperatures which are most important in the present comparison (50–100°K), dispersion is important and $E(i)/E_0$, where E_0 is the total thermal energy, is a complicated function of temperature. Therefore Mason and Bateman's nonlinearity parameter D should be a function of temperature.

A second problem is the neglect of the \mathbf{k} dependence of the Grüneisen constants and the relaxation time.

¹² Bommel and Dransfeld's result differs from Woodruff and Ehrenreich's equation primarily in that $\Omega^2\tau/(1+\Omega^2\tau^2)$ appears rather than $\frac{1}{2}\tan^{-2}\Omega\tau$. The first form can be obtained from the Woodruff and Ehrenreich formalism by setting the group velocity of all modes to zero. The second form results from setting the group velocity of all modes equal to the velocity of the sound wave. Neither is strictly correct for real solids, and the difference is negligible only if $\Omega\tau \ll 1$.

¹³ B. N. Brockhouse, Phys. Rev. Letters 2, 256 (1959); B. N. Brockhouse and P. K. Iyengar, Phys. Rev. 111, 747 (1958).

¹⁴ H. Palevsky, D. J. Hughes, W. Kley, and E. Tunkels, Phys. Rev. Letters 2, 258 (1959).

Bienenstock¹⁵ has calculated $\gamma(\mathbf{k}\mu)$ for germanium and found that there is a strong dispersion, with $\gamma^2(\mathbf{k},\text{TA})$ going to zero about half-way to the zone boundary and then increasing again out to the boundary. The neglect of the k dependence of $\tau(\mathbf{k}\mu)$ is also questionable, but difficult to avoid.

The combined effect of these simplifications can qualitatively account for the discrepancy between the Bommel-Dransfeld formula and the experimental data for Si and Ge. The specific heat, thermal conductivity, and ultrasonic attenuation each involve a different type of average over \mathbf{k} and μ :

$$C_V = \sum_{\mathbf{k}\mu} C(\mathbf{k}\mu), \quad (39)$$

$$A \propto \sum_{\mathbf{k}\mu} C(\mathbf{k}\mu)\tau(\mathbf{k}\mu)\{[\gamma(\mathbf{k}\mu)]^2 - \gamma_i^2\}, \quad (40)$$

and

$$\kappa = \frac{1}{3} \sum_{\mathbf{k}\mu} C(\mathbf{k}\mu)[v_{\theta}(\mathbf{k}\mu)]^2\tau(\mathbf{k}\mu). \quad (41)$$

A is from Woodruff and Ehrenreich's formulation. The term γ_i^2 comes from $\Delta T/T$ and is small for a longitudinal strain wave and absent for a transverse wave. $v_{\theta}(\mathbf{k}\mu)$ is the group velocity of mode $(\mathbf{k}\mu)$. The separate roles played by normal, umklapp, and impurity scattering in κ are neglected, and each mode is characterized by a single $\tau(\mathbf{k}\mu)$.

All three sums, C_V , A , and κ , are probably dominated by the TA branch. For C_V , the TA contribution in the low-temperature limit is about 16 times the LA contribution. At higher temperatures, the difference is less, but the strong TA dispersion accentuates that mode and should make it dominate up to an appreciable fraction of the Debye temperature.

Holland⁹ has shown, on the basis of a curve-fitting procedure, that the TA modes carry the majority of the heat in Si and Ge. A similar conclusion was reached by Parrot *et al.*¹⁶ While this position is not definitely established, it is a reasonable hypothesis. If $\tau(\mathbf{k},\text{TA})$ is large enough to dominate κ in spite of the small $v_{\theta}(\mathbf{k},\text{TA})$ at large k , then the TA modes must also dominate A , since the Grüneisen constants are not that different for the two modes.

With these assumptions, we can qualitatively explain the fact that Bommel and Dransfeld's formula predicts too rapid an increase in A with increasing T in the 25–75°K range. As T is increased, the total specific heat of the TA branch increases rapidly as TA modes of larger \mathbf{k} become populated. However, these modes have smaller values of γ^2 than do the TA modes near $\mathbf{k} = 0$, and the average γ^2 decreases with T . Therefore, the use of experimental specific-heat data with a temperature-independent Grüneisen constant must predict¹⁷ too

¹⁵ A. Bienenstock, Phil. Mag. 9, 755 (1964).

¹⁶ J. E. Parrot, Proc. Phys. Soc. (London) 81, 726 (1961); R. A. H. Hamilton and J. E. Parrot, Phys. Rev. 178, 1284 (1969).

¹⁷ B. I. Miller, Phys. Rev. 132, 2477 (1963).

rapid an increase of A with T . In other words, Mason and Bateman's use of the more weakly temperature-dependent function, E_0 rather than $C_V T$ compensates for their neglect of the temperature dependence of γ^2 and leads to a fortuitous agreement with experiment.

Of course, the above gives no consideration to the \mathbf{k} dependence of τ . It might be argued that the use of τ_{th} is not a bad approximation if TA modes dominate both κ and A , since in both cases $\tau(\mathbf{k}, \text{TA})$ is weighted with a decreasing function of k , viz., v_g^2 for κ and γ^2 for A . One difficulty with this argument is that $[\gamma(\mathbf{k}, \text{TA})]^2$ is large again near the zone boundary, whereas $v_g \rightarrow 0$ there. Therefore some error would be expected at temperatures high enough for the zone boundary modes to be populated.

For completeness the problems involved in obtaining τ_{th} , apart from those in interpreting τ_{th} , should be pointed out. The thermal conductivity data used by Mason and Bateman was obtained on different samples than those used in obtaining the ultrasonic attenuation data. This practice can lead to errors, since small numbers of impurities and imperfections can alter the thermal conductivity of semiconductors drastically.^{18,19} In Ge, this effect is usually not important above 50°K so that the relaxation times obtained from the thermal conductivity data are indicative of the material and not the particular sample in that temperature range. In Si, however, the situation is quite different, and impurity effects influence the thermal conductivity^{19,20} to temperatures above 100°K so that the same samples should be used in measuring ultrasonic attenuation and thermal conductivity. Furthermore, the Si data used by Mason and Bateman are more indicative of data obtained on very impure material and at 100°K is a

¹⁸ J. H. Carruthers, T. H. Geballe, H. M. Rosenberg, and J. J. Ziman, Proc. Roy. Soc. (London) **238**, 502 (1957).

¹⁹ M. G. Holland and L. J. Neuringer, in *Proceedings of the International Conference on the Physics of Semiconductors, Exeter, 1962* (The Institute of Physics and the Physical Society, London, 1962), p. 475.

²⁰ C. J. Glassbrenner and G. A. Slack, Phys. Rev. **134**, A1058 (1964).

factor of 2 lower than the majority of published data on the material.²⁰ The room-temperature values of thermal conductivity are, however, correct, implying some inconsistency in the temperature dependence of the relaxation time or the remaining terms in the theory.

In summary, it has been shown that there are inconsistencies in the development of the Mason-Bateman theory and further difficulties in adapting the theory to Si and Ge. Most of the more rigorous theories of ultrasonic attenuation are too complex and contain too many unknowns to make them useful in fitting experimental data, even when such well-characterized materials as Si and Ge are under study. The use of simplifying assumptions is almost inevitable, and the best approach at present seems to be to use the theories to find trends in attenuation from material to material,²¹ or to help explain the variation of attenuation with impurity or defect concentrations.^{8,22} In addition, the use of Grüneisen parameters derived from third-order elastic constants, in a manner analogous to Mason and Bateman's work, may prove fruitful in understanding the dependence of ultrasonic attenuation or propagation and polarization direction in a given material.

Note added in manuscript. Following completion of this manuscript, a recent paper by R. N. Thurston [Sixth International Congress on Acoustics, Tokyo, August, 1968 (unpublished)] came to the authors' attention. In this paper it is also shown that the attenuation involves the specific heat times the temperature rather than thermal energy. The authors are grateful to Dr. Mason for pointing out this work.

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²¹ D. W. Oliver and G. A. Slack, J. Appl. Phys. **37**, 1542 (1966).

²² B. D. Silverman, Progr. Theoret. Phys. (Kyoto) **39**, 245 (1968).