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Lowest-Order Nonvanishing Contribution to Lattice Viscosity*

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The lowest-order nonvanishing contribution to the viscosity of a crystal lattice is considered. This contribution depends on the cubic anharmonic momentum-flux operator previously derived by the author. An inhomogeneous transport equation, which describes both anharmonic and imperfection phonon scattering and whose solution determines the viscosity, is presented. The scattering operator is then replaced by a single-relaxation-time approximation where the effective relaxation time is found from lattice-thermal-conductivity experiments. With the aid of a Debye-like model, solutions are obtained for the coefficients of viscosity. From these solutions the attenuations of longitudinal and transverse sound waves are calculated and compared with experiment for Ge and Si, where qualitative agreement is found.

I. INTRODUCTION

NONEQUILIBRIUM statistical mechanics gives us expressions for such transport coefficients as the thermal conductivity, viscosity, and coefficients of diffusion. The transport relations, which incorporate these coefficients (e.g., Fourier's law of heat conduction), together with the macroscopic conservation laws form the hydrodynamic equations of motion. Here, the term hydrodynamic refers to processes which can be described in terms of a limited class of macroscopic variables such as the local energy density, particle number density, momentum density, etc., or equivalently, local thermodynamic variables such as the temperature, chemical potential, velocity, etc.

It has been shown that the transport coefficients are given by time integrals of correlation functions involving the microscopic fluxes. This formulation is valid for all phases of matter. For a complete discussion see McLennan,[1] and DeVault and McLennan.[2] To reduce the correlation-function formulas of a solvable form, one is confronted with a many-body problem. For example, for a gas one attempts to reduce the formula to a sum of quantities which involve the motion of a single particle. For a dielectric crystal it is convenient to reduce the formula to a sum of quantities involving a single phonon mode. Even with these simplifications the problem is still rather formidable; however, one is in a position to make meaningful approximations.

Starting with the kinetic theory of Peierls[3] and more recently with the correlation-function treatment of Hardy *et al.*,[4–6] the theory of lattice thermal conductivity has been discussed in considerable detail. Hardy, Swenson, and Schieve[5] give a perturbation expansion for the thermal conductivity. The Hamiltonian for the lattice is written as $H^0+\lambda H'$, where H^0 is the harmonic Hamiltonian for a perfect lattice and $\lambda H'$ is the perturbation due to anharmonic forces and lattice imperfections. The lowest-order term in the perturbation expansion is of order λ^{-2}. The λ^{-1}-order corrections have been treated in detail by Hardy and Schieve.[6]

Some confusion appears to exist concerning what is meant by the viscosity of a crystal. To make the concept clear consider the macroscopic conservation laws for a system with one atomic constituent,

$$\frac{\partial\rho}{\partial t}+\nabla\cdot\mathbf{j}=0, \tag{1.1}$$

$$\frac{\partial u}{\partial t}+\nabla\cdot\mathbf{s}=0, \tag{1.2}$$

$$\frac{\partial p_i}{\partial t}+\frac{\partial t_{ij}}{\partial x_j}=0, \tag{1.3}$$

where ρ, u, $\mathbf{p}$ are the densities of mass, energy, and momentum and $\mathbf{j}$, $\mathbf{s}$, t_{ij} are the associated fluxes. The energy flux for slowly varying hydrodynamic processes can be written as[1]

$$s_i=s_i{}^0-\lambda_{ij}\partial T/\partial x_j. \tag{1.4}$$

$s_i{}^0$ is the reversible part of the energy flux, which is zero for a system with a vanishing local velocity. λ_{ij} is the thermal conductivity and can be determined from its correlation-function formula. Similarly the momentum flux or pressure tensor can be written as

$$t_{ij}=t_{ij}{}^0-\tfrac{1}{2}\eta_{ijlm}\left[\frac{\partial v_l}{\partial x_m}+\frac{\partial v_m}{\partial x_l}\right], \tag{1.5}$$

where $\mathbf{v}$ is the local velocity. $t_{ij}{}^0$ is the reversible part of the pressure tensor which in general is not zero even for systems with vanishing local velocity. The coefficient η_{ijlm} is the viscosity and can be determined for any phase of matter from its correlation-function expression. In a solid the symmetric part of the velocity gradient is often referred to as the strain rate.

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[1] J. A. McLennan, in *Advances in Chemical Physics*, edited by I. Prigogine (John Wiley & Sons, Inc., New York, 1963), Vol. V.

[2] G. P. DeVault and J. A. McLennan, Phys. Rev. **137**, A724 (1965).

[3] R. E. Peirels, Ann. Physik 3, 1055 (1929).

[4] R. J. Hardy, J. Math. Phys. **6**, 1749 (1965); **7**, 1435 (1966).

[5] R. J. Hardy, R. J. Swenson, and W. C. Schieve, J. Math. Phys. **6**, 1741 (1965).

[6] R. J. Hardy and W. C. Schieve, J. Math. Phys. **7**, 1439 (1966).

Just as a temperature gradient will disrupt the equilibrium phonon distribution of a crystal, so will a velocity gradient. In fact, it has been shown[7] that the disturbance of the phonons caused by a velocity gradient does lead to a finite viscosity. The lowest order (λ^{-2}) contribution to the viscosity was discussed in Ref. 7; however, it has recently been shown[8] that the diagonal part of the harmonic part of the momentum-flux operator, which was used there, actually vanishes identically with the result[9] that the λ^{-2} contribution to the viscosity also vanishes. (Although the derivation of the harmonic momentum-flux operator in Ref. 7 was in error, the remaining conclusions cited there are correct.) The λ^{-1}-order contributions also vanish since each of the six possible contributions at this order also depends on the diagonal part of the harmonic part of the momentum-flux operator being nonzero.

The lowest-order nonvanishing contribution to the viscosity comes from the λ^0 order of the perturbation expansion. There are six possible contributions at the λ^0 order. It was shown in the preceding paper[9] that five of these are zero. Here we treat the remaining nonvanishing contribution which depends on the diagonal elements of the anharmonic momentum-flux operator. This operator has been derived in an earlier paper.[8]

In Sec. II the inhomogeneous transport equation whose solution determines the viscosity is discussed, and the collision operator is replaced by a single-relaxation-time approximation. Since the collision operator is the same as that for thermal conductivity, the effective relaxation time is obtained for particular materials from thermal conductivity experiments. The results of Sec. II are used in Sec. III to compute the coefficients of viscosity by employing a Debye-like model for a primitive lattice with a cubic symmetry. Both an approximate analytic solution and a numerical solution (by use of a computer) are obtained for germanium and silicon. It is interesting to note that, in a sense, lattice viscosity depends more strongly on the anharmonicities than does the lattice thermal conductivity. Both the homogeneous and the inhomogeneous parts of the transport equation for the viscosity are involved with the anharmonicities. This will be shown to mean effectively that in considering the damping of an infinitesimal strain sound wave one must use finite strain to determine the viscosity.

In Sec. IV the viscosity is used to determine the attenuation of longitudinal and transverse sound waves in germanium and silicon. Comparison is made with experimental results reported by Mason and Bateman[10] and qualitative agreement is found. The conclusion previously suggested by Mason and Bateman[10] and by Klemens[11] that the relaxation time associated with longitudinal wave attenuation should be about twice that of thermal conductivity seems reasonable here. The results are discussed in Sec. V.

The Appendix discusses a simple model for extending the present analysis to describe materials which exhibit viscoelastic behavior, i.e., materials which "remember" their past history.[2]

II. THE TRANSPORT EQUATION

It was shown in Sec. III of Ref. 9 (the preceding paper) that the lowest-order nonvanishing contribution to the coefficients of viscosity for a lattice is given by

$$\eta_{ijlm}=V^{-1}\sum_{\mathbf{k}s}\hbar\omega_{\mathbf{k}s}[\gamma_{\mathbf{k}s}{}^{ij}-V(\partial\langle\lambda T_{ij}'\rangle^0/\partial\langle H^0\rangle^0)]\varphi_{\mathbf{k}s}{}^{lm}, \tag{2.1}$$

where $\lambda T_{ij}'$ is the perturbation to the volume-averaged momentum-flux operator $T_{ij}=T_{ij}{}^0+\lambda T_{ij}'$, $T_{ij}{}^0$ is the harmonic part of the flux, and $\lambda T_{ij}'$ is due to anharmonic forces and lattice imperfections. The same separation occurs for the system Hamiltonian $H=H^0+\lambda H'$, where H^0 is the harmonic Hamiltonian. The brackets $\langle\ \rangle^0$ imply an average taken with the unperturbed-equilibrium canonical ensemble $f_0{}^0$. The quantities $\omega_{\mathbf{k}s}$ and $\gamma_{\mathbf{k}s}{}^{ij}$ are, respectively, the frequency and generalized Grüneisen parameters associated with mode $(\mathbf{k},s)$.[8] V is the volume of the system. $\varphi_{\mathbf{k}s}{}^{lm}$ is defined by

$$\varphi_{\mathbf{k}s}{}^{lm}\equiv(V/\kappa T)\sum_{\alpha\beta}f_0{}^0(\alpha)N_{\mathbf{k}s}(\alpha)\times[\lambda T_{lm}'(\beta)-\lambda\hat{T}_{lm}'(\beta)]\tilde{P}_\epsilon(\alpha\beta), \tag{2.2}$$

where the diagonal elements of an operator in the phonon representation are denoted by, for example, $f_0{}^0(\alpha)\equiv\langle\alpha|f_0{}^0|\alpha\rangle$. The time average of $\lambda T_{lm}'$ is denoted by $\lambda\hat{T}_{lm}'$.[9] $\tilde{P}_\epsilon(\alpha\beta)$ is the lowest order perturbation approximation to the Laplace transform of the transition probability $|\langle\alpha|\exp(-iHt/\hbar)|\beta\rangle|^2$; $N_{\mathbf{k}s}$ is the phonon number operator associated with mode $(\mathbf{k},s)$; and T and κ are, respectively, the temperature and Boltzmann's constant. $\varphi_{\mathbf{k}s}{}^{lm}$ satisfies the transport equation

$$T\frac{d\langle N_{\mathbf{k}s}\rangle^0}{dT}\left(\gamma_{\mathbf{k}s}{}^{lm}-V\frac{\partial\langle\lambda T_{lm}'\rangle^0}{\partial\langle H^0\rangle^0}\right)=L[\varphi_{\mathbf{k}s}{}^{lm}], \tag{2.3}$$

where the operator L describes the effect of the scattering of the phonons due to anharmonic forces and lattice imperfections, and is given by the right side of Eq. (4.49) in Ref. 7.

We note that as was discussed in Ref. 9, Eqs. (2.1), (2.2), and (2.3) depend only on the diagonal part of $\lambda T_{ij}'$. Only the cubic anharmonic part of the perturbation contributes to the diagonal part and thus[8]

$$\lambda T_{lm}'(\beta)=V^{-1}\sum_{\mathbf{k}s}\hbar\omega_{\mathbf{k}s}[N_{\mathbf{k}s}(\beta)+\tfrac{1}{2}]\gamma_{\mathbf{k}s}{}^{lm}. \tag{2.4}$$

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[7] G. P. DeVault and J. A. McLennan, Phys. Rev. **138**, A856 (1965).

[8] G. P. DeVault, Phys. Rev. **149**, 624 (1966).

[9] G. P. DeVault and R. J. Hardy, preceding paper, Phys. Rev. **155**, 869 (1967).

[10] W. P. Mason and T. B. Bateman, J. Acoust. Soc. Am. **36**, 644 (1964).

[11] P. G. Klemens, in *Physical Acoustics*, edited by W. P. Mason (Academic Press Inc., New York, 1965), Vol. 3.

The quantity $\varphi_{\mathbf{k}s}{}^{lm}$ bears a close relation to the nonequilibrium ensemble f for the system. For the process we are considering, f is given by[7]

$$\begin{aligned} f&=f_L+Df_0\\ &=f_L-\frac{V}{\kappa T}\frac{\partial v_l}{\partial x_m}\int_0^\infty dt\, e^{-\epsilon t}[T_{lm}(-t)-\hat{T}_{lm}]f_0, \end{aligned}\tag{2.5}$$

where f_L is the local equilibrium ensemble and f_0 is the strict equilibrium ensemble. To the order of perturbation we are considering,

$$\begin{aligned} f(\alpha)=f_L(\alpha)-\frac{V}{\kappa T}\frac{\partial v_l}{\partial x_m}f_0{}^0(\alpha)&\\ \times\sum_\beta[\lambda T_{lm}'(\beta)-\lambda\hat{T}_{lm}'(\beta)]\tilde{P}_\epsilon(\alpha\beta)&. \end{aligned}\tag{2.6}$$

By forming the average of the number operator with (2.6) we find

$$\begin{aligned} \langle N_{\mathbf{k}s}\rangle&=\sum_\alpha f(\alpha)N_{\mathbf{k}s}(\alpha)\\ &=\langle N_{\mathbf{k}s}\rangle_L-\frac{\partial v_l}{\partial x_m}\varphi_{\mathbf{k}s}{}^{lm}, \end{aligned}\tag{2.7}$$

indicating the relation between $\varphi_{\mathbf{k}s}{}^{lm}$ and the deviation of the average number of phonons in mode $(\mathbf{k},s)$ from the local equilibrium average.

Also by using (2.6), the expression (2.1) for the viscosity can be simplified. From the definition of thermodynamic variables for the nonequilibrium state[1] one has the condition that the average energy density must be equal to the local equilibrium average. This condition, together with (2.6), leads to

$$\sum_{\mathbf{k}s}\hbar\omega_{\mathbf{k}s}\varphi_{\mathbf{k}s}{}^{lm}=0.\tag{2.8}$$

Thus (2.1) can be simplified to

$$\eta_{ijlm}=V^{-1}\sum_{\mathbf{k}s}\hbar\omega_{\mathbf{k}s}\gamma_{\mathbf{k}s}{}^{ij}\varphi_{\mathbf{k}s}{}^{lm}.\tag{2.9}$$

Equation (2.9), in conjunction with the solution of the transport equation (2.3), then determines the viscosity.

Relaxation-Time Model

By using the local equilibrium ensemble[1] one can show to the order of approximation we are considering that

$$\begin{aligned} \frac{d\langle N_{\mathbf{k}s}\rangle_L}{dt}=\frac{V}{\kappa T}\sum_\beta f_0{}^0(\beta)N_{\mathbf{k}s}(\beta)&\\ \times[\lambda T_{lm}'(\beta)-\lambda\hat{T}_{lm}'(\beta)]\frac{\partial v_l}{\partial x_m}&. \end{aligned}\tag{2.10}$$

We now assume that $\langle N_{\mathbf{k}s}\rangle$ relaxes according to

$$\left.\frac{d\langle N_{\mathbf{k}s}\rangle}{dt}\right|_{\text{collisions}}=\frac{\langle N_{\mathbf{k}s}\rangle_L-\langle N_{\mathbf{k}s}\rangle}{\tau_c},\tag{2.11}$$

where τ_c is a combined relaxation time for normal and umklapp processes, and imperfection scattering. Then by combining (2.11), (2.10), (2.7), and (2.4) the integral equation (2.3) takes the form

$$\frac{d\langle N_{\mathbf{k}s}\rangle_L}{dt}=\left.\frac{d\langle N_{\mathbf{k}s}\rangle}{dt}\right|_{\text{collisions}},\tag{2.12}$$

or

$$T\frac{d\langle N_{\mathbf{k}s}\rangle^0}{dT}\left(\gamma_{\mathbf{k}s}{}^{lm}-V\frac{\partial\langle\lambda T_{lm}'\rangle^0}{\partial\langle H^0\rangle^0}\right)=\frac{1}{\tau_c}\varphi_{\mathbf{k}s}{}^{lm}.\tag{2.13}$$

Thus the solution to the relaxation equation is

$$\varphi_{\mathbf{k}s}{}^{lm}=\tau_c T\frac{d\langle N_{\mathbf{k}s}\rangle^0}{dT}\left(\gamma_{\mathbf{k}s}{}^{lm}-V\frac{\partial\langle\lambda T_{lm}'\rangle^0}{\partial\langle H^0\rangle^0}\right).\tag{2.14}$$

The possibility that solutions to the homogeneous part of the integral equation (2.3) should be added to the solution (2.14) must be considered. However, such solutions are multiplied by constants which are to be determined. Condition (2.8) serves to show that the homogeneous solution proportional to $\hbar\omega_{\mathbf{k}s}$ (which exists for all processes considered here) is not to be included in (2.14). Furthermore, it is obvious that the homogeneous solution linear in $\mathbf{k}$ (which exists for normal processes only) does not contribute to the viscosity since (2.9) is only sensitive to the part of $\varphi_{\mathbf{k}s}{}^{lm}$ which is an even function of $\mathbf{k}$. It was pointed out in Ref. 7 that, in principal, a finite viscosity exists even when only normal processes are considered. In contrast to these remarks, in lattice thermal conductivity one cannot treat normal processes alone; furthermore, in the conductivity treatment of more general processes which include normal processes, the homogeneous solution linear in $\mathbf{k}$ must be included.[12]

Debye Model

In order to be able to explicitly calculate the coefficients of viscosity, we now consider a Debye-like model of the lattice. From the expressions (2.9) and (2.14) the coefficients of viscosity are

$$\begin{aligned} \eta_{ijlm}=V^{-1}T\sum_{\mathbf{k}s}\tau_c(\mathbf{k}s)\mathcal{C}_{\mathbf{k}s}\gamma_{\mathbf{k}s}{}^{ij}&\\ \times(\gamma_{\mathbf{k}s}{}^{lm}-V\partial\langle\lambda T_{lm}'\rangle^0/\partial\langle H^0\rangle^0)&, \end{aligned}\tag{2.15}$$

where

$$\mathcal{C}_{\mathbf{k}s}=\hbar\omega_{\mathbf{k}s}\frac{d\langle N_{\mathbf{k}s}\rangle^0}{dT};\tag{2.16}$$

$\mathcal{C}_{\mathbf{k}s}$ is a heat capacity associated with the mode $(\mathbf{k},s)$. Since the collision operator L is the same as that of the

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[12] J. Callaway, Phys. Rev. **113**, 1046 (1959); P. G. Klemens, Proc. Roy. Soc. (London) **208**, 108 (1951).

lowest-order contribution to the thermal conductivity,[4] we will use the relaxation time τ_c obtained from thermal conductivity experiments on cubic crystals. In particular, we use the effective temperature-dependent relaxation time defined through

$$\lambda = \tfrac{1}{3}\tau_c C_V c^2, \tag{2.17}$$

where λ is the thermal conductivity, C_V is the specific heat per unit volume,[13] and c is the Debye-averaged sould speed. The resulting τ_c is taken independent of $\mathbf{k}s$ but, obviously, is temperature-dependent.

Further, we use the long-wave limit for the pressure tensor as discussed in Ref. 8,

$$\langle \lambda T_{ij}' \rangle^0 = V^{-1} \langle H^0 \rangle^0 \gamma^{ij}, \tag{2.18}$$

where

$$\gamma^{ij} = (12\pi)^{-1} \int d\Omega \sum_s \gamma_{\mathbf{k}s}{}^{ij}, \tag{2.19}$$

and $d\Omega$ is an element of solid angle in $\mathbf{k}$ space. The Grüneisen parameters, in the long-wave limit,[8]

$$\gamma_{\mathbf{k}s}{}^{ij} = -e_{\mathbf{k}s}{}^{i} e_{\mathbf{k}s}{}^{j} - \tfrac{1}{2} \sum_{lmpr} e_{\mathbf{k}s}{}^{l} e_{\mathbf{k}s}{}^{p} (k_m k_r / \rho \omega_{\mathbf{k}s}{}^2) \times [c_{ijlmpr} + c_{ijmr}\delta_{lp}], \tag{2.20}$$

are assumed not to depend on the magnitude of $\mathbf{k}$ but rather only on the direction $\hat{k} = \mathbf{k}/k$. The c_{ijmr} and c_{ijlmpr} are the second- and third-order elastic constants.

Also, all polarizations are considered to contribute equally to the total specific heat when weighted with the Debye-averaged sound speed. With these assumptions and

$$V^{-1} \sum_{\mathbf{k}} \rightarrow (2\pi)^{-3} \int dk\, k^2 \int d\Omega, \tag{2.21}$$

one can re-express (2.15) as follows:

$$\eta_{ijlm} = \tau_c T C_V \left\{ (12\pi)^{-1} \int d\Omega \sum_s \gamma_{ks}{}^{ij} \gamma_{ks}{}^{lm} - \gamma^{ij}\gamma^{lm} \right\}. \tag{2.22}$$

III. EVALUATION OF VISCOSITY COEFFICIENTS

We ultimately wish to compare the results of the evaluation of (2.22) with the results from experimental measurements of attenuation of sound waves in cubic crystals. There are three independent second-order elastic constants and six independent third-order elastic constants for crystals with cubic symmetry.[14] It might be thought that the easiest way to approximate the very complicated integrals involved in (2.22) would be to assume spherical symmetry. For the case of spherical symmetry there are two independent second-order elastic constants and three independent third-order elastic constants. To approximate cubic symmetry by spherical symmetry there must then exist certain relations[14] between the elastic constants. Although these relations concerning the second-order constants are reasonably well satisfied for such cubic crystals as Ge and Si, the relations concerning the third-order constants are not at all well satisfied. We must preserve the anisotropy of the crystal.

We now proceed to discuss a computer calculation of the integrals involved in Eq. (2.22) for the coefficients of viscosity. It is convenient to define

$$I_{ijlm} \equiv (12\pi)^{-1} \int d\Omega \sum_s \gamma_{ks}{}^{ij} \gamma_{ks}{}^{lm}, \tag{3.1}$$

so that (2.22) becomes

$$\eta_{ijlm} = \tau_c T C_V (I_{ijlm} - \gamma^{ij}\gamma^{lm}). \tag{3.2}$$

For cubic symmetry there are three independent coefficients of viscosity. For our purposes it is sufficient to calculate two of them. Using the abbreviated notation[14] for the coefficients of viscosity and elasticity we consider

$$\eta_{11} = \tau_c T C_V (I_{11} - \gamma^2), \tag{3.3}$$

$$\eta_{44} = \tau_c T C_V I_{44}, \tag{3.4}$$

where γ is the Grüneisen constant defined by

$$\gamma = \tfrac{1}{3} \sum_i \gamma^{ii} = (36\pi)^{-1} \int d\Omega \sum_i \sum_s \gamma_{ks}{}^{ii}. \tag{3.5}$$

The polarization vectors $\mathbf{e}_{ks}$ are chosen so that they form a mutually orthogonal basis with the longitudinal polarization in the direction of $\mathbf{k}$. It is convenient for the purpose of the solid-angle integration to make the arbitrary choice of taking one of the transverse polarization vectors to be in the azimuthal plane.

The third-order elastic constants have recently been measured at room temperature for germanium and silicon.[15] By using these values together with the measured second-order elastic constant,[16] calculations performed on an IBM 7094 computer gave the results:

for Ge,

$$\gamma = 0.742, \quad I_{11} = 1.035, \quad I_{44} = 0.1259; \tag{3.6}$$

for Si,

$$\gamma = 0.491, \quad I_{11} = 0.682, \quad I_{44} = 0.0795. \tag{3.7}$$

An estimate of the validity of these calculations can be obtained by comparing the calculated Grüneisen constants with the experimental values as obtained from

$$\gamma = \alpha K / C_V, \tag{3.8}$$

where α is the volume thermal expansion coefficient and

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[13] By specific heat per unit volume we mean the specific heat per unit mass multiplied by the density. By context the thermal conductivity λ is not to be confused with the perturbation strength.

[14] R. N. Thurston and K. Brugger, Phys. Rev. 133, A1604 (1964).

[15] H. J. McSkimin and P. Andreatch, Jr., J. Appl. Phys. 35, 3312 (1964).

[16] H. J. McSkimin and P. Andreatch, Jr., J. Appl. Phys. 34, 651 (1963); 35, 2161 (1964).

K is the bulk modulus defined by

$$K=\tfrac{1}{9}\sum_{ij} c_{iijj}=\tfrac{1}{3}(c_{11}+2c_{12}). \qquad (3.9)$$

By using the thermal data compiled by Corruccini and Gniewek[17] for α and C_V, one obtains $\gamma=0.75$ for Ge and $\gamma=0.41$ for Si at room temperature. The agreement is very good for Ge but rather poor for Si. However, the thermal data compiled by Gschneidner[18] yield $\gamma=0.56$ for Si. The computed value (3.7) of γ for Si is equal to the mean of the two experimental values.

The calculated results (3.6) and (3.7) will be used in in the next section in computing the attenuation of longitudinal and transverse sound waves. First, however, we turn to an approximate hand calculation of I_{11}, I_{44}, and γ. The results of these calculations will indicate the dependence of the viscosity on the elastic constants. The basis of these calculations is the approximation which results from ignoring any polarization dependence in the denominators in (2.20) and (2.22). The following replacement is made:

$$k^2/\rho\omega_{\mathbf{k}s}^2=1/\rho\hat{c}^2; \qquad (3.10)$$

$\hat{c}$ is a velocity chosen such that the Grüneisen constant (3.5) will be equal to the value calculated on a computer. One obtains

$$I_{11}=\frac{11}{45}+\frac{1}{315}\frac{1}{\rho\hat{c}^2}[35(c_{11}+2c_{12})+23c_{111}+8c_{112}+4c_{123}+8c_{144}+62c_{166}]+\frac{1}{7560}\frac{1}{\rho^2\hat{c}^4}[84(3c_{11}+2c_{12})(c_{111}+2c_{166})$$
$$+168(c_{11}+4c_{12})(c_{112}+c_{144}+c_{166})+126(3c_{11}^2+4c_{11}c_{12}+8c_{12}^2)+2c_{111}(43c_{111}+16c_{144}+32c_{112}+100c_{166}+8c_{123})$$
$$+4c_{144}(57c_{144}+61c_{112}+58c_{166}+15c_{123})+c_{112}(369c_{112}+440c_{166}+38c_{123})+4c_{166}(149c_{166}+8c_{123})+57c_{123}^2], \qquad (3.11)$$

$$I_{44}=\frac{2}{45}+\frac{1}{630}\frac{1}{\rho\hat{c}^2}(9c_{144}+47c_{166}+18c_{456})+\frac{1}{3780}\frac{1}{\rho^2\hat{c}^4}[252c_{44}^2+168c_{44}(2c_{166}+c_{456})$$
$$+c_{144}(29c_{144}+46c_{166}+74c_{456})+c_{166}(269c_{166}+118c_{456})+116c_{456}^2], \qquad (3.12)$$

and

$$\gamma=-\frac{1}{3}-\frac{1}{18}\frac{1}{\rho\hat{c}^2}[3(c_{11}+2c_{12})+(c_{111}+4c_{166}+2c_{112}+2c_{144})]. \qquad (3.13)$$

For Ge, (3.11) and (3.12) reduce to

$$I_{11}=1.230, \quad I_{44}=0.289, \qquad (3.14)$$

and agree sufficiently well with (3.6) and (3.11) and (3.12) may be useful in indicating the effect on the viscosity if future measurements report changes in the elastic constants.

IV. ATTENUATION

Necessary for a discussion of the attenuation of a sound wave are the macroscopic conservation laws (1.1)–(1.3). For linear slowly varying processes they can be reduced to, with the aid of standard thermodynamic relations,

$$C_\epsilon\frac{\partial T}{\partial t}+\tfrac{1}{3}T\alpha_{ij}c_{ijlm}\frac{\partial \epsilon_{lm}}{\partial t}=\lambda_{ij}\frac{\partial^2 T}{\partial x_i\partial x_j}, \qquad (4.1)$$

$$\rho\frac{\partial^2 u_i}{\partial t^2}+\frac{\partial t_{ij}}{\partial x_j}=0, \qquad (4.2)$$

where

$$t_{ij}=\tfrac{1}{3}\alpha_{lm}(T-T_0)c_{ijlm}-c_{ijlm}\epsilon_{lm}-\eta_{ijlm}\partial\epsilon_{lm}/\partial t, \qquad (4.3)$$

and where summation over repeated subscripts is understood. Here, C_ϵ is the specific heat per unit volume at constant strain; α_{ij}, the thermal expansion coefficient tensor; ϵ_{ij}, the infinitesimal strain tensor; λ_{ij}, the thermal conductivity tensor; **u**, the displacement vector; T, the temperature; and T_0, the reference temperature. For crystals with cubic symmetry

$$\alpha_{is}=\alpha\delta_{ij}, \quad \lambda_{ij}=\lambda\delta_{ij}. \qquad (4.4)$$

Substitution of a transverse wave traveling in the 1 direction and polarized in the 2 direction leads to a dispersion relation in terms of the wave number and the frequency. For the boundary-value problem this is solved for the wave number in terms of the frequency and to lowest order in the frequency the imaginary part of the wave number, i.e., the attenuation with distance, is

$$\Gamma_T=(\omega^2/2\rho c_T^3)\eta_{44}, \qquad (4.5)$$

where ω is the angular frequency of the wave and c_T is the transverse wave velocity. The next term in the expansion is of order ω^4 and is negligible for the frequencies being considered here.

Similarly, a longitudinal wave in the 1 direction yields for the attenuation

$$\Gamma_L=(\omega^2/2\rho c_L^3)(\eta_{11}+\lambda T\gamma^2/c_L^2), \qquad (4.6)$$

where c_L is the longitudinal wave velocity.

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[17] R. J. Corruccini and J. J. Gniewek, Natl. Bur. Std. (U. S.) Monograph **21**, (1960); **29** (1961).

[18] K. A. Gschneidner, Jr., in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1964), Vol. 16.

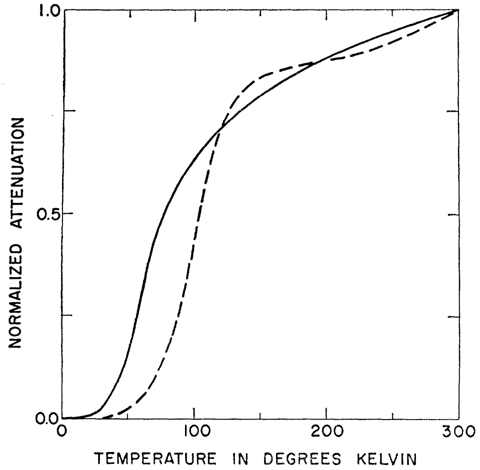

FIG. 1. Measured and calculated longitudinal attenuation in Ge normalized to unity at 300°K. Experimental measurements are represented by solid line.

By expressing (4.5) and (4.6) in terms of I_{11} and I_{44} with the aid of (2.17) we obtain

$$\Gamma_T = (\omega^2/2\rho c_T^3)\tau_c T C_V I_{44}, \tag{4.7}$$

$$\Gamma_L = (\omega^2/2\rho c_L^3)\tau_c T C_V \{I_{11} - [1-\tfrac{1}{3}(c/c_L)^2\gamma^2]\}. \tag{4.8}$$

The temperature-dependent relaxation time was obtained from the thermal conductivity experiments of Geballe and Hull[19] with one exception. Following the suggestion of Klemens[11] and of Mason and Bateman,[10] the relaxation time for η_{11} was given twice this value thereby effectively doubling the I_{11} in Eq. (4.8). Then, by using the results calculated for I_{11}, I_{44}, and γ which are given by (3.6) and (3.7), the measured specific heats,[17] and the measured second-order elastic constants,[16] the longitudinal and transverse attenuations can be compared with experiment. The results of these calculations are compared with the experimental results of Mason and Bateman[10] for $T = 300$°K in Table I. The numbers in parentheses in Table I are the frequencies of the sound waves in Mc/sec. Table I indicates that both the calculated longitudinal and transverse attenuations are about 50% lower than the experimental values. The ratio Γ_L/Γ_T calculated here, however, is very close to the experimental ratio.

Only a qualitative discussion of the temperature dependence of the attenuation can be given. This is because the integrals involved in the definitions of I_{11}, I_{44}, and γ depend on the third-order elastic constants which have only been measured at $T = 300$°K. However, the experimental Grüneisen constants as computed from (3.8) for Ge and Si show a marked temperature dependence indicating that the third-order elastic constants are highly temperature-dependent. Since the integrands of I_{11} and I_{44} are quadratic in the Grüneisen parameters, we can attempt to obtain a qualitative indication of the temperature dependence of the attenuation by assuming that the temperature dependence of the Grüneisen parameters $\gamma_{ks}{}^{ij}$ is that of the experimental Grüneisen constant γ. One expects that such an approximation will be better for I_{11} than for I_{44} since I_{11} depends on $\gamma_{ks}{}^{11}$ and I_{44} depends on $\gamma_{ks}{}^{12}$, i.e., since $\gamma = \gamma^{11}$ and $\gamma^{12} = 0$ for cubic symmetry. A comparison between the temperature dependence calculated in this way and as determined from experiment is given in Fig. 1 for longitudinal attenuation in Ge.

TABLE I. Theoretical and experimental attenuation.

	Γ_L (dB/cm)	Γ_T (dB/cm)	Γ_L/Γ_T
Ge (calc.)	1.34 (306)	0.42 (306)	3.2
Ge (expt.)	2.75 (306)	0.73 (306)	3.8
Si (calc.)	1.18 (480)	0.33 (495)	3.6
Si (expt.)	2.2 (480)	0.62 (495)	3.5

The limitation of this approximation can be seen from the following: For transverse waves the experimental attenuation does not decrease nearly as rapidly with decreasing temperature so that the preceding approximation is not an accurate portrayal. Furthermore, for Si the thermal expansion coefficient vanishes at about 120°K, indicating by this approximation that the attenuation should vanish at 120°K. This is not observed.

V. DISCUSSION

There have been earlier treatments of the attenuation of sound waves in solids in which it was realized that a sound wave will disturb the equilibrium phonon distribution thereby causing entropy production as the system tends to return to equilibrium.[20] Such treatments are generally based on the use of a Boltzmann transport equation to determine the attenuation due to viscosity. However, as was discussed in Ref. 7, since the momentum is not transported with the phonon group velocity it is not obvious from the kinetic-theory viewpoint how to formulate the correct transport equation. The result of these analyses was that totally unrealistic values for the Grüneisen constants were necessary to bring about agreement with experiment.

Mason and Bateman[10] have developed an ingenious heuristic model for the attenuation which has some similarities with the results of this paper. Their development is based on assuming the medium is viscoelastic (see Appendix) so that the medium has a memory. An essential difference, though, is that their end result depends on the thermal energy (multiplied by a factor of 3) rather than $C_V T$.[21] This together with the viscoelastic assumption yields a temperature dependence

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[19] T. H. Geballe and G. W. Hull, in *Low Temperature Physics and Chemistry*, edited by J. R. Dillinger (University of Wisconsin Press, Madison, Wisconsin, 1958), Paper No. 42-6.

[20] A. Akhieser, J. Phys. (USSR) **1**, 277 (1939); H. E. Bömmel and K. Dransfeld, Phys. Rev. **117**, 1245 (1960); T. O. Woodruff and H. Ehrenreich, *ibid.* **123**, 1553 (1961).

[21] See Ref. 10, Eq. (25).

which agrees quite well with their experimental results for both longitudinal and transverse attenuation. However, they assume the Grüneisen constants to be temperature-independent which clearly is not the case. There is a need for further experimental work.

The approach used here and in the preceding paper, i.e., a perturbation expansion of the correlation-function expression for the viscosity, leads in a systematic way to the correct transport equation at any given order of the perturbation. At the lowest nonvanishing order, meaningful approximations were applied and qualitative agreement with experiment was determined *without the use of any adjustable parameters.* The longitudinal attenuation was found to be due to both viscosity and thermal conductivity, and the transverse attenuation due to viscosity alone. One cannot properly categorize the part of the longitudinal attenuation due to thermal conductivity as being due to viscoelasticity as was attempted in the past.[22]

A deviation from the quadratic dependence of the attenuation on ω is observed at low temperatures.[10] Viscoelasticity, which is treated in terms of a simple model in the Appendix, gives such a deviation. However, this could possibly be explained by boundary scattering of the phonons, to which the hydrodynamic theory presented here does not apply. Also it is possible that a low temperatures $\omega\tau_c$ is sufficiently large compared with unity that the lowest order in the Chapman-Enskog expansion of the nonequilibrium system ensemble, which is considered in the present theory, is not sufficient.

Besides the transport coefficients of thermal conductivity and viscosity, there is also the possibility of cross terms in the relations between the macroscopic fluxes and forces (gradients). That is, the energy flux might have a term proportional to the velocity gradient and the momentum flux a term proportional to the temperature gradient. The associated transport coefficients would then be tensors of rank three which must vanish for cubic symmetry. A more general analysis indicates that these coefficients must also vanish for more complicated symmetries (at least at the order of perturbation we have considered). This is due to the result that, for the case of the momentum flux, the coefficients are sensitive only to the even part in $\mathbf{k}$ of the solution of the proper transport equation. However, this transport equation yields only solutions which are odd in $\mathbf{k}$.

APPENDIX

A brief discussion of a simple model of viscoelasticity is given here. In the event that the medium is characterized by large internal relaxation times, i.e., of the order of or greater than times characterizing hydrodynamic rates of change, then Eq. (1.5) for the local macroscopic pressure tensor is replaced by[2]

$$t_{ij}(\mathbf{x},t)=t_{ij}{}^{0}(\mathbf{x},t)-\int_{-\infty}^{t}dt'\,K_{ijlm}(t-t')\partial v_l(\mathbf{x},t')/\partial x_m\,,\quad \text{(A1)}$$

where the relaxation function is given by

$$K_{ijlm}(t)=(V/\kappa T)\langle T_{ij}(t)[T_{lm}-\hat{T}_{lm}]\rangle_0\,.\quad \text{(A2)}$$

Basic properties of the relaxation functions have been discussed in Ref. 2.

Consider the Fourier transform of Eq. (A1),

$$\begin{aligned}t_{ij}(\mathbf{x},\omega)&=\int_{-\infty}^{\infty}dt\,e^{i\omega t}t_{ij}(\mathbf{x},t)\\&=t_{ij}{}^{0}(\mathbf{x},\omega)-K_{ijlm}(\omega)\partial v_l(\mathbf{x},\omega)/\partial x_m\,,\quad \text{(A3)}\end{aligned}$$

where $K_{ijlm}(\omega)$ is the Laplace transform

$$\begin{aligned}K_{ijlm}(\omega)&=\int_{0}^{\infty}dt\,e^{i\omega t}K_{ijlm}(t)\\&=(V/\kappa T)\int_{0}^{\infty}dt\,e^{i\omega t}\langle T_{ij}(t)[T_{lm}-\hat{T}_{lm}]\rangle_0\,.\quad \text{(A4)}\end{aligned}$$

Note that in the limit $\omega\rightarrow 0$, $K_{ijlm}(\omega)\rightarrow\eta_{ijlm}$, $K_{ijlm}(t)\rightarrow\eta_{ijl}\delta(t)$, and Eq. (A1) reduces to (1.5). Thus, while for ordinary viscosity we only had to consider a single number for a particular coefficient of viscosity, we now are faced with determining a complete spectrum.

A simple model is to use the Markoffian Pauli equation in conjunction with (A4) to determine $K_{ijlm}(\omega)$, the net result being non-Markoffian from the hydrodynamic point of view. However, we must now keep the term in the Pauli equation which vanished in the limit $\omega\rightarrow 0$ (see Ref. 7). Then following the procedure outlined in Sec. II of this paper, we find

$$K_{ijlm}(\omega)=V^{-1}\sum_{\mathbf{k}s}\hbar\omega_{\mathbf{k}s}\gamma_{\mathbf{k}s}{}^{ij}\varphi_{\mathbf{k}s}{}^{lm}(\omega)\,,\quad \text{(A5)}$$

where

$$\varphi_{\mathbf{k}s}{}^{lm}(\omega)=\frac{\tau_c T}{1-i\omega\tau_c}\frac{d\langle N_{\mathbf{k}s}\rangle^0}{dT}\left(\gamma_{\mathbf{k}s}{}^{lm}-V\frac{\partial\langle\lambda T_{lm}{}'\rangle^0}{\partial\langle H^0\rangle^0}\right).\quad \text{(A6)}$$

Thus, by assuming an effective relaxation time independent of $\mathbf{k}$,

$$K_{ijlm}(\omega)=(1-i\omega\tau_c)^{-1}\eta_{ijlm}\,.\quad \text{(A7)}$$

Inversion of the Laplace transform yields

$$K_{ijlm}(t)=(1/\tau_c)e^{-t/\tau_c}\eta_{ijlm}\,.\quad \text{(A8)}$$

We note that this relaxation function represents what

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[22] K. Lucke, J. Appl. Phys. 27, 1453 (1956).

the spring and dashpot people call a standard linear solid.

In the limit $\tau_c \to 0$, $\tau_c^{-1}\exp(-t/\tau_c)$ can be considered as a representation of $\delta(t)$ in the sense

$$\lim_{\tau_c\to 0}\frac{1}{\tau_c}\int_0^\infty dt\, e^{-t/\tau_c}f(t)=f(0)\,, \qquad \text{(A9)}$$

by a well-known property of Laplace transform theory. Therefore as $\tau_c \to 0$, the model approaches ordinary viscosity.

The relaxation function (A8) modifies the expressions (4.5) and (4.6) for the transverse and longitudinal attenuations by multiplying them by a factor $(1+\omega^2\tau_c^2)^{-1}$.

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Temperature Dependence of the Width of the Fundamental Lattice-Vibration Absorption Peak in Ionic Crystals. II. Approximate Numerical Results

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The results of numerical calculations of the temperature dependence of the width and position of the fundamental lattice-vibration absorption peak in NaCl and LiF are presented. The calculations are carried out in the high-temperature limit, on the basis of the Hardy-Karo deformation dipole model of these crystals. Cubic and quartic anharmonic terms are retained in the crystal Hamiltonian, but the approximation of neglecting the anharmonicity of the Coulomb forces has been made. The expressions for the Fourier-transformed anharmonic force constants have been approximated and simplified by a method suggested by Peierls. The results of the calculations show that the quartic anharmonic terms in the crystal potential energy make a contribution to the width of the fundamental absorption peak which is comparable in magnitude with the contribution from the cubic anharmonic terms, in agreement with the theoretical arguments of Gurevich and Ipatova. Since the quartic anharmonic contribution to the width is proportional to the square of the absolute temperature at high temperatures, these results provide an explanation for the experimental observations that the width increases with a power of the absolute temperature which is intermediate between the first and the second. Quantitatively, the theoretical results are in quite good agreement with the experimental data of Heilmann for the variation with temperature of the width of the fundamental absorption peak in LiF. In the case of NaCl, the agreement between theory and experiment is somewhat poorer, but the theoretical values are still within a factor of about 2 of the experimental values of Hass. The frequency dependence of the imaginary part of the dielectric constant of these two crystals has also been calculated, and is compared with experimental data.

1. INTRODUCTION

IN the first part of this series[1] a formal expression for the imaginary part of the dielectric constant of an ionic crystal of the rocksalt structure was derived. It has the form

$$\varepsilon_2(\omega)=\frac{4\pi\epsilon^2}{V_a}\frac{M_+ + M_-}{M_+M_-}\times\frac{2\omega_t\Gamma_t(\omega)}{[\omega^2-\Omega_t^2(\omega)]^2+4\omega_t^2\Gamma_t^2(\omega)}\,. \qquad (1.1)$$

In this expression ϵ is the first-order dipole-moment expansion coefficient, V_a is the volume of a primitive unit cell, and M_+ and M_- are the masses of the positive and negative ions, respectively. The frequency of the incident light is denoted by ω, and ω_t is the frequency of the transverse optical modes of infinite wavelength. Explicit expressions for the renormalized frequency $\Omega_t(\omega)$ and the damping constant $\Gamma_t(\omega)$ were obtained to second order in the cubic and quartic anharmonic force constants in I. It was shown there as well that the coefficient $(4\pi\epsilon^2/V_a)(M_+ + M_-)/M_+M_-$ can be identified with $(\varepsilon_0-\varepsilon_\infty)\omega_0^2$, where ε_0 and ε_∞ are the static and

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[1] I. P. Ipatova, A. A. Maradudin, and R. F. Wallis, Fiz. Tverd. Tela 8, 1064 (1966) [English transl.: Soviet Phys.—Solid State 8, 850 (1966)]. This paper will be referred to as I, and all references to equations from this paper will be prefixed by I.