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Acoustic Attenuation by Neutral Donor Impurity Atoms in Germanium

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We study the attenuation of phonons at low temperature by neutral donor impurity atoms in germanium. Keyes as well as Griffin and Carruthers have calculated the attenuation due to elastic-phonon scattering by trapped electrons. They applied their results to thermal phonons and obtained good agreement with thermal-conductivity measurements. However, recent experiments in acoustic-phonon attenuation indicate a much larger attenuation than that predicted by their calculation. It is shown here that the observed attenuation can be explained by other processes that dominate at low or acoustic frequencies, namely, inelastic scattering and thermally assisted absorption. Attenuation of phonons by resonance absorption is also considered using the thermodynamic Green's-function technique.

I. INTRODUCTION

RECENTLY Pomerantz[1] measured the attenuation of transverse acoustic phonons at the microwave frequency $\omega=2\pi\times 9\times 10^9\ \mathrm{sec}^{-1}$ in slightly doped n-type germanium (impurity density $\simeq 10^{15}\ \mathrm{cm}^{-3}$) in the temperature range 5 to 40°K. He observed that the attenuation is much larger than in pure germanium. Since at such temperatures nearly all the electrons are trapped by the donor atoms, the additional attenuation must be due to the neutral impurity atoms. Keyes[2] as well as Griffin and Carruthers[3] have calculated the attenuation due to elastic phonon scattering off the electrons in the donor levels. Their result, however, is too small to account for the observed acoustic-phonon attenuation. In this paper other allowed processes are considered. We find that the attenuation due to inelastic phonon scattering and thermally assisted absorption provides good agreement with the experimental data.

In Sec. II the interaction between electrons in the donor atoms and phonons is discussed. In Sec. III the phonon attenuation coefficients due to the various allowed processes in the second Born approximation are calculated and the results compared with experiments. Finally, in Sec. IV the attenuation of phonons with frequencies in resonance with the impurity levels are calculated by Green's-function techniques.

II. INTERACTION BETWEEN PHONONS AND ELECTRONS IN DONOR IMPURITY ATOMS

We will now consider the interaction between the phonons and the electrons in the neutral donor atoms. Since the impurity concentration is small, we may consider one atom at a time. The total attenuation is then the product of the attenuation coefficient due to one atom and N_i, the impurity concentration.

The total Hamiltonian of the system (with one impurity atom) is

$$H=H_e+H_{\mathrm{ph}}+H_{e-\mathrm{ph}}. \qquad (1)$$

In second quantized notation we have

$$\begin{aligned} H_e&=\sum_n \epsilon_n c_n{}^\dagger c_n\,,\\ H_{\mathrm{ph}}&=\tfrac{1}{2}\sum_{\mathbf{q}\lambda}\hbar\omega_{\mathbf{q}\lambda}(a_{\mathbf{q}\lambda}a_{\mathbf{q}\lambda}{}^\dagger+a_{\mathbf{q}\lambda}{}^\dagger a_{\mathbf{q}\lambda})\,, \qquad (2)\\ H_{e-\mathrm{ph}}&=\sum_{nn'\mathbf{q}\lambda}\Xi_{n'n}{}^\lambda(\mathbf{q})c_{n'}{}^\dagger c_n(\hbar\omega_{\mathbf{q}\lambda}/2\rho c_{\mathbf{q}\lambda})^{1/2}(a_{\mathbf{q}\lambda}+a_{\mathbf{q}\lambda}{}^\dagger)\,, \end{aligned}$$

where c_n and $c_n{}^\dagger$ are the electron annihilation and creation operators for the level n with energy ϵ_n; $a_{\mathbf{q}\lambda}$ and $a_{\mathbf{q}\lambda}{}^\dagger$ are the annihilation and creation operators for the phonon in the λ branch with wave vector $\mathbf{q}$, sound velocity $c_{\mathbf{q}\lambda}$, and frequency $\omega_{\mathbf{q}\lambda}=c_{\mathbf{q}\lambda}q$; ρ is the mass density; and $\Xi_{n'n}{}^\lambda(\mathbf{q})$ are the deformation-potential matrix elements. We have not put in explicitly the electron-electron interaction that would exclude the possibility of having more than one electron in the atom. The operators in Eq. (2) satisfy the usual commutation relations, i.e.,

$$\begin{gathered} c_nc_{n'}{}^\dagger+c_{n'}{}^\dagger c_n=\delta_{nn'}\,,\\ c_nc_{n'}+c_{n'}c_n=0\,,\\ c_n{}^\dagger c_{n'}{}^\dagger+c_{n'}{}^\dagger c_n{}^\dagger=0\,, \end{gathered}$$

and (3)

$$\begin{gathered} a_{\mathbf{q}\lambda}a_{\mathbf{q}'\lambda'}{}^\dagger-a_{\mathbf{q}'\lambda'}{}^\dagger a_{\mathbf{q}\lambda}=\delta_{\mathbf{q}\mathbf{q}'}\delta_{\lambda\lambda'}\,,\\ a_{\mathbf{q}\lambda}a_{\mathbf{q}'\lambda'}-a_{\mathbf{q}'\lambda'}a_{\mathbf{q}\lambda}=0\,,\\ a_{\mathbf{q}\lambda}{}^\dagger a_{\mathbf{q}'\lambda'}{}^\dagger-a_{\mathbf{q}'\lambda'}{}^\dagger a_{\mathbf{q}\lambda}{}^\dagger=0\,. \end{gathered}$$

Let us now review the level structure of a shallow donor atom in germanium. The hydrogenic ground state in the effective-mass approximation is four-fold degenerate because of the four equivalent conduction-band minima.[4] This degeneracy is partially removed if valley-orbit coupling is taken into account.[4] A singlet ground state is separated from the remaining degenerate triplet states. The energy separation is known as the chemical shift and is usually denoted by 4Δ. The values of 4Δ for the various n-type impurities are given in

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[1] M. Pomerantz, Proc. IEEE **53**, 1438 (1965); and to be published.

[2] R. W. Keyes, Phys. Rev. **122**, 1171 (1961).

[3] A. Griffin and P. Carruthers, Phys. Rev. **131**, 1976 (1963).

[4] W. Kohn, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5, p. 257.

TABLE I. Values of 4Δ for the various n-type impurities.

Donor	Sb	P	As
$4\Delta/k_B$ °K	3.7	33	49

Table I.[5] The higher energy levels are ~ 50°K above the triplet states. We will neglect all such levels in the following calculation because in thermal equilibrium in the temperature range of interest ($T<40$°K) it is a reasonable approximation to assume that only the singlet and triplet states are occupied. The deformation-potential matrix elements $\Xi_{n'n}{}^{\lambda}(\mathbf{q})$ for these states are known and can be expressed in the following form[6]:

$$\Xi_{n'n}{}^{\lambda}(\mathbf{q})=\hat{\epsilon}_i(\mathbf{q},\lambda)\hat{q}_j(\Xi_d\delta_{ij}\delta_{n'n}+\tfrac{1}{3}\Xi_u D_{ij}{}^{n'n})F(q)$$

or

$$=\tilde{\Xi}_{n'n}{}^{\lambda}(\hat{q})F(q)$$

$$(n;n')=(\text{singlet; triplet}), \tag{4}$$

where $\hat{\epsilon}(\mathbf{q},\lambda)$ is a polarization vector and $\hat{q}$ is the unit vector along $\mathbf{q}$; Ξ_d and Ξ_u are the deformation potentials defined by Herring,[7]

$$\begin{matrix}\Xi_d\cong-8\text{ eV}\\ \Xi_u\cong19\text{ eV}\end{matrix}\quad\text{for}\quad\text{Ge}^{8}; \tag{5}$$

$F(q)$ is a form factor given approximately by[9]

$$F(q)\cong(1+\tfrac{1}{4}a^{*2}q^2)^{-2}, \tag{6}$$

where a^* is roughly equal to the Bohr radius of the impurity atom ($\sim 3\times10^{-7}$ cm) and the matrices $D_{ij}{}^{n'n}$ are defined as

$$D_{ij}{}^{n'n}=3\sum_{v=1}^{4}\hat{a}_i{}^{(v)}\hat{a}_j{}^{(v)}\alpha_{n'}{}^{(v)}\alpha_n{}^{(v)}. \tag{7}$$

The summation in Eq. (7) goves over the four valleys of the conduction band, the bottoms of which are located along the unit vectors $\hat{a}^{(v)}$. In the Cartesian coordinate system with the (1,0,0) orthogonal axes as reference, these vectors are

$$\hat{a}^{(v)}=1/\sqrt{3}(1,1,1);\quad 1/\sqrt{3}(-1,1,1);\quad 1/\sqrt{3}(1,-1,1);$$
$$1/\sqrt{3}(-1,-1,1)\quad\text{for}\quad(v)=1,2,3,4. \tag{8}$$

The constants $\alpha_n{}^{(v)}$ are the coefficients introduced[10] to describe the linear combination of the four Bloch states at the conduction-band minima forming the singlet and triplet states. Denoting the singlet state by 0 and the triplet states by (1,2,3) we have

TABLE II. Matrices $D_{ij}{}^{nn'}$.

$$\begin{aligned}
&D_{ij}{}^{00}=D_{ij}\\
&D_{ij}{}^{01}=D_{ij}{}^{10}=D_{ij}{}^{1}\\
&D_{ij}{}^{02}=D_{ij}{}^{20}=D_{ij}{}^{2}\\
&D_{ij}{}^{03}=D_{ij}{}^{30}=D_{ij}{}^{3}\\
&D_{ij}{}^{11}=D_{ij}+D_{ij}{}^{3}\\
&D_{ij}{}^{12}=D_{ij}{}^{21}=0\\
&D_{ij}{}^{13}=D_{ij}{}^{31}=D_{ij}{}^{1}\\
&D_{ij}{}^{22}=D_{ij}-D_{ij}{}^{3}\\
&D_{ij}{}^{23}=D_{ij}{}^{32}=-D_{ij}{}^{2}\\
&D_{ij}{}^{33}=D_{ij}{}^{00}
\end{aligned}$$

$$D_{ij}=\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix};\quad D_{ij}{}^{1}=\frac{1}{\sqrt{2}}\begin{pmatrix}0&0&1\\0&0&1\\1&1&0\end{pmatrix};\quad D_{ij}{}^{2}=\frac{1}{\sqrt{2}}\begin{pmatrix}0&0&-1\\0&0&1\\-1&1&0\end{pmatrix}$$

$$\text{and}\quad D_{ij}{}^{3}=\begin{pmatrix}0&1&0\\1&0&0\\0&0&0\end{pmatrix}$$

$$\begin{aligned}
\alpha_0{}^{(v)}&=\tfrac{1}{2}(1,1,1,1),\\
\alpha_1{}^{(v)}&=1/\sqrt{2}(1,0,0,-1),\\
\alpha_2{}^{(v)}&=1/\sqrt{2}(0,1,-1,0),\\
\alpha_3{}^{(v)}&=\tfrac{1}{2}(1,-1,-1,1).
\end{aligned} \tag{9}$$

Using Eqs. (8) and (9) we obtain Table II for the matrices $D_{ij}{}^{nn'}$.[11] From Table II we observe that the diagonal deformation-potential matrix element $\Xi_{00}{}^{\lambda}(\mathbf{q})$ is nonzero only for $\lambda=$ longitudinal mode, and is given by

$$\Xi_{00}{}^{\lambda=l}(\mathbf{q})=(\Xi_d+\Xi_u/3)F(q). \tag{10}$$

III. CALCULATION OF PHONON ATTENUATION COEFFICIENTS

In this section the electron-phonon Hamiltonian $H_{\text{e-ph}}$ given in Eq. (2) is used to calculate the phonon attenuation coefficients. As mentioned before, we will only retain the terms $n, n'=$ (single; triplet) $=(0;1,2,3)$ in the Hamiltonian. We further assume that there is no local strain in the crystal.

First of all, we calculate the attenuation using perturbation theory. As long as the energy of the acoustic phonon $\hbar\omega_{\mathbf{q}\lambda}$ is not equal to 4Δ, the attenuation in the first Born approximation which corresponds to the process[12]

$$\hbar\omega_{\mathbf{q}\lambda}+(\text{singlet})\rightleftarrows(\text{triplet}) \tag{11a}$$

is zero because energy cannot be conserved. We must go to the next order in the perturbation calculation, the second Born approximation. Let us remark that near resonance, i.e., $\hbar\omega_{\mathbf{q}\lambda}\simeq4\Delta$, the perturbation calculation fails as the succeeding terms in the perturbation series become comparable or even larger in magnitude. To get meaningful results, one must perform a selective sum

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[5] J. H. Reuszer and P. Fisher, Phys. Rev. **135**, A1125 (1964).

[6] H. Hasegawa, Phys. Rev. **118**, 1513 (1960).

[7] C. Herring and E. Vogt, Phys. Rev. **101**, 944 (1956).

[8] See for example R. W. Keyes, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 11, p. 149.

[9] For a detailed discussion see Ref. 6.

[10] W. Kohn and J. M. Luttinger, Phys. Rev. **98**, 915 (1955).

[11] In Ref. 6, only the matrices D^{00}, D^{01}, D^{02}, and D^{03} are evaluated.

[12] By the symbol (triplet) we mean any one of the triplet states,

of the series, or, equivalently, take the widths of the levels into account. One may think of the attenuation at resonance being given by the following "process":

$$\hbar\omega_{\mathbf{q}\lambda}+(\text{singlet})^{*}\rightleftarrows(\text{triplet})^{*}, \tag{11b}$$

where the asterisk indicates that the width of the level is included. The calculation of the attenuation coefficient for such situations will be discussed in the next section. At present we will consider the attenuation of phonons whose frequencies $\omega_{\mathbf{q}\lambda}$ are such that a perturbation calculation is valid. One condition on $\omega_{\mathbf{q}\lambda}$ is seen to be

$$|\hbar\omega_{\mathbf{q}\lambda}-4\Delta|\gg\Gamma_0+\Gamma, \tag{12a}$$

where Γ_0 and Γ are the level widths of the singlet and the triplet states arising from the interaction with the thermal phonons. They are of the same order as the energy splittings of the triplet states by the thermal phonons (expressions will be given in the next section). There is another condition on the frequency; namely,

$$\hbar\omega_{\mathbf{q}\lambda}\gg\Gamma_0,\ \Gamma. \tag{12b}$$

The reason is that, for frequencies which do not satisfy (12b), the attenuation is described by the processes

$$\begin{aligned}\hbar\omega_{q\lambda}+(\text{singlet})^{*}&\rightleftarrows(\text{singlet})^{*}\\ \hbar\omega_{q\lambda}+(\text{triplet})^{*}&\rightleftarrows(\text{triplet})^{*},\end{aligned} \tag{13}$$

for which perturbation theory fails to apply. These cases are also discussed in Sec. IV.

We will now calculate the phonon attenuation in the second Born approximation, which is valid when Eqs. (12a) and (12b) are satisfied. There are three distinct types of allowed processes and they are treated separately below.

A. Elastic Scattering

This is the process previously considered by Keyes,[2] and Griffen and Carruthers.[3] It may be written symbolically as

$$\begin{aligned}\hbar\omega_{\mathbf{q}\lambda}+(\text{singlet})&\rightleftarrows(\text{Int.})\rightleftarrows\hbar\omega_{\mathbf{q}'\lambda'}+(\text{singlet}),\\ \hbar\omega_{\mathbf{q}\lambda}+(\text{triplet})&\rightleftarrows(\text{Int.})\rightleftarrows\hbar\omega_{\mathbf{q}'\lambda'}+(\text{triplet}),\end{aligned} \tag{14}$$

where (Int.) denotes the appropriate intermediate states. The attenuation coefficient $\alpha_{\mathbf{q}\lambda}$ for the phonon $(\mathbf{q},\lambda)$ is defined as $1/c_{\mathbf{q}\lambda}\tau_{\mathbf{q}\lambda}$, where $\tau_{\mathbf{q}\lambda}$ is the phonon life time. Following standard procedure[13] we obtain

$$\alpha_{\mathbf{q}\lambda}{}^{(a)}=\frac{\pi}{2\rho c_{\mathbf{q}\lambda}{}^{3}}\omega_{\mathbf{q}\lambda}\sum_{n}f_n(T)\sum_{\mathbf{q}'\lambda'}\frac{\omega_{\mathbf{q}'\lambda'}}{\rho c_{\mathbf{q}'\lambda'}{}^{2}}\delta(\omega_{\mathbf{q}\lambda}-\omega_{\mathbf{q}'\lambda'})\times\sum_{\substack{n'\\(\epsilon_n=\epsilon_{n'})}}\left|\sum_{m}\left(\frac{\Xi_{n'm}{}^{\lambda'}(\mathbf{q}')\Xi_{mn}{}^{\lambda}(\mathbf{q})}{\epsilon_m-\epsilon_n-\hbar\omega_{\mathbf{q}\lambda}}+\frac{\Xi_{n'm}{}^{\lambda}(\mathbf{q})\Xi_{mn}{}^{\lambda'}(\mathbf{q}')}{\epsilon_m-\epsilon_n+\hbar\omega_{\mathbf{q}\lambda}}\right)\right|^{2}, \tag{15}$$

where the superscript (a) refers to the particular process under consideration and n, m, and n' refer to the initial, intermediate, and final electronic states, respectively. The factor $f_n(T)$ is the thermal-equilibrium population at temperature T of the level n, which is assumed to satisfy a Boltzmann distribution, i.e.,

$$f_n(T)=Ae^{-(\epsilon_n/k_BT)};\quad A=\text{const}. \tag{16a}$$

We will denote the singlet state population by $f_0(T)$ and that of a triplet state by $f(T)$. We will assume that they satisfy

$$f_0(T)+3f(T)=1. \tag{16b}$$

Let us discuss briefly the behavior of attenuation $\alpha_{\mathbf{q}\lambda}{}^{(a)}$ for low frequencies such that $\hbar\omega_{\mathbf{q}\lambda}\ll4\Delta$. This condition is satisfied for all types of impurity as long as $\omega_{\mathbf{q}\lambda}\ll4\times10^{11}$ sec^{-1} (which corresponds to the smallest 4Δ in Table I). In this case the sum inside the absolute-value sign is dominated by those terms[14] with $\epsilon_m=\epsilon_n$, unless they cancel exactly. The remaining terms are smaller by a factor of $\hbar\omega_{\mathbf{q}\lambda}/4\Delta$. If we neglect corrections of order $\hbar\omega/4\Delta$ and replace the sound velocities $c_{\mathbf{q},\lambda}$ by their angular averages c_λ we find that $\alpha_{\mathbf{q}\lambda}{}^{(a)}$ is

$$\alpha_{\mathbf{q}\lambda}{}^{(a)}=\frac{f_0(T)}{4\pi\rho c_\lambda{}^3}\omega_{q\lambda}{}^2\frac{1}{\hbar^2}\left(\frac{\hbar\omega_{q\lambda}}{4\Delta}\right)^2F^2(q)\sum_{\lambda'}\frac{4}{\rho c_{\lambda'}{}^5}F^2\left(\frac{c_\lambda}{c_{\lambda'}}q\right)\left\langle\!\left\langle\left|\sum_{m=1,2,3}\tilde{\Xi}_{0m}{}^{\lambda'}(\hat{q}')\tilde{\Xi}_{m0}{}^{\lambda}(\hat{q})\right|^2\right\rangle\!\right\rangle$$
$$+\frac{f(T)}{4\pi\rho c_\lambda{}^3}\omega_{q\lambda}{}^2\frac{1}{\hbar^2}F^2(q)\sum_{\lambda'}\frac{1}{\rho c_{\lambda'}{}^5}F^2\left(\frac{c_\lambda}{c_{\lambda'}}q\right)\left\langle\!\left\langle\sum_{\substack{n,n'=1,2,3\\(n\neq n')}}\left|\sum_{m=1,2,3}\left(\tilde{\Xi}_{n'm}{}^{\lambda'}(\hat{q}')\tilde{\Xi}_{mn}{}^{\lambda}(\hat{q})-\tilde{\Xi}_{n'm}{}^{\lambda}(\hat{q})\tilde{\Xi}_{mn}{}^{\lambda'}(\hat{q}')\right)\right|^2\right\rangle\!\right\rangle, \tag{17}$$

where the symbol $\langle\langle\ \rangle\rangle$ means an angular average over $\hat{q}'$. Thus the first term, which represents elastic scattering off the singlet state, is proportional to the population of this state and the phonon frequency to the fourth power. The form factors are essentially unity since $a^*q=a^*(\omega_{q\lambda}/c_\lambda)\ll1$ for the phonons under consideration. The second term, corresponding to elastic scattering off the triplet states, is proportional to the population of these states and the square of the phonon frequency. The ratio of the first term to the second term is, upon using Eq. (16a),

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[13] See for example, L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955).

[14] In Ref. 3, Griffin and Carruthers have omitted all these terms since they have used only the deformation-potential matrix elements between the singlet and singlet state and the singlet and triplet states.

of the order

$$e^{4\Delta/k_BT}(\hbar\omega_{q\lambda}/4\Delta)^2. \tag{18}$$

For example, for $\hbar\omega_{q\lambda}=\frac{1}{10}4\Delta$, the temperature below which the first term dominates is $\sim\frac{1}{5}(4\Delta/k_B)$.

We will now study two processes that have not been previously considered.

B. Inelastic Scattering

By inelastic phonon scattering we mean the following process:

$$\hbar\omega_{\mathbf{q}\lambda}+(\text{triplet})\leftrightarrows(\text{int.})\leftrightarrows\hbar\omega_{\mathbf{q}'\lambda'}+(\text{singlet}). \tag{19}$$

The acoustic phonon is inelastically scattered into a high-energy phonon ($\hbar\omega_{\mathbf{q}'\lambda'}\simeq 4\Delta$) while the electron jumps down from the triplet to the singlet state. The attenuation coefficient for the phonon $\omega_{\mathbf{q}\lambda}$ denoted by $\alpha_{\mathbf{q}\lambda}{}^{(b)}$ is readily calculated to be

$$\alpha_{\mathbf{q}\lambda}{}^{(b)}=\frac{\pi}{2\rho c_\lambda{}^3}\omega_{q\lambda}(1-e^{-(\hbar\omega_{q\lambda}/k_BT)})f(T)F^2(q)\sum_{\mathbf{q}'\lambda'}\frac{\omega_{q'\lambda'}}{\rho c_{\lambda'}{}^2}(1+n_{\mathbf{q}'\lambda'})\delta\left(\omega_{\mathbf{q}'\lambda'}-\frac{4\Delta}{\hbar}-\omega_{\mathbf{q}\lambda}\right)F^2(q')$$
$$\times\sum_{n=1,2,3}\left|\sum_m\left(\frac{\tilde{\Xi}_{0m}{}^{\lambda'}(\hat{q}')\tilde{\Xi}_{mn}{}^{\lambda}(\hat{q})}{\epsilon_m-\epsilon_n-\hbar\omega_{q\lambda}}+\frac{\tilde{\Xi}_{0m}{}^{\lambda}(\hat{q})\Xi_{mn}{}^{\lambda'}(\hat{q}')}{\epsilon_m-\epsilon_0+\hbar\omega_{q\lambda}}\right)\right|^2, \tag{20}$$

where $n_{\mathbf{q}'\lambda'}$ is the phonon-distribution function

$$n_{\mathbf{q}'\lambda'}=(e^{\hbar\omega_{\mathbf{q}'\lambda'}/k_BT}-1)^{-1}=n(\omega_{\mathbf{q}'\lambda'}). \tag{21}$$

We have, for simplicity, neglected the angular dependence of the phonon velocities. When $\hbar\omega_{q\lambda}\ll 4\Delta$ we find that $\alpha_{\mathbf{q}\lambda}{}^{(b)}$ is adequately described by

$$\alpha_{\mathbf{q}\lambda}{}^{(b)}=\frac{f(T)}{4\pi\rho c_\lambda{}^3}\frac{1}{\hbar k_BT}F^2(q)\sum_{\lambda'}\frac{1}{\rho c_{\lambda'}{}^5}\left(\frac{4\Delta}{\hbar}\right)^3\left(1+n\left(\frac{4\Delta}{\hbar}\right)\right)F^2\left(\frac{4\Delta}{\hbar c_{\lambda'}}\right)$$
$$\times\langle\langle\sum_{n=1,2,3}|\sum_{m=1,2,3}(\tilde{\Xi}_{0m}{}^{\lambda'}(\hat{q}')\tilde{\Xi}_{mn}{}^{\lambda}(\hat{q}))-\tilde{\Xi}_{00}{}^{\lambda}(\hat{q})\tilde{\Xi}_{0n}{}^{\lambda'}(\hat{q}')|^2\rangle\rangle, \tag{22}$$

where we have approximated $[1-\exp(-\hbar\omega_{q\lambda}/k_BT)]$ by $\hbar\omega_{q\lambda}/k_BT$ since, for acoustic frequencies, $\hbar\omega_{q\lambda}$ is also much less than k_BT. Thus the attenuation is independent of frequency and proportional to the population of the triplet state divided by the temperature (neglecting the phonon distribution function $n(4\Delta/\hbar)$. Upon comparing Eq. (22) with Eq. (17) we find that the ratio $\alpha_{q\lambda}{}^{(b)}/\alpha_{q\lambda}{}^{(a)}$ is

$$\frac{\alpha_{q\lambda}{}^{(b)}}{\alpha_{q\lambda}{}^{(a)}}\cong e^{-(4\Delta/k_BT)}\left(\frac{4\Delta}{k_BT}\right)\left(\frac{4\Delta}{\hbar\omega_{q\lambda}}\right)^4F^2\left(\frac{4\Delta}{\hbar c}\right)\quad\text{for}\quad e^{4\Delta/k_BT}\left(\frac{\hbar\omega_{q\lambda}}{4\Delta}\right)^2>1$$
$$\cong\left(\frac{4\Delta}{k_BT}\right)\left(\frac{4\Delta}{\hbar\omega_{q\lambda}}\right)^2F^2\left(\frac{4\Delta}{\hbar c}\right)\quad\text{for}\quad e^{4\Delta/k_BT}\left(\frac{\hbar\omega_{q\lambda}}{4\Delta}\right)^2<1. \tag{23}$$

We can easily see that for most acoustic-phonon frequencies, except at low temperature, the attenuation due to inelastic scattering $\alpha_{q\lambda}{}^{(b)}$ dominates.

C. Absorption

We will now consider the last type of allowed processes in the second Born approximation, which will be called the thermally assisted phonon-absorption process

$$\hbar\omega_{\mathbf{q}\lambda}+\hbar\omega_{\mathbf{q}'\lambda'}+(\text{singlet})\leftrightarrows(\text{int.})\leftrightarrows(\text{triplet}), \tag{24}$$

where $\hbar\omega_{\mathbf{q}'\lambda'}$ is a thermal phonon. The attenuation due to this process is

$$\alpha_{\mathbf{q}\lambda}{}^{(c)}=\frac{\pi}{2\rho c_\lambda{}^3}\omega_{q\lambda}(1-e^{-(\hbar\omega_{q\lambda}/k_BT)})f_0(T)F^2(q)\sum_{\mathbf{q}'\lambda'}\frac{\omega_{\mathbf{q}'\lambda'}}{\rho c_{\lambda'}{}^2}n_{\mathbf{q}'\lambda'}\delta\left(\omega_{\mathbf{q}'\lambda'}-\frac{4\Delta}{\hbar}+\omega_{q\lambda}\right)F^2(q')$$
$$\times\sum_{n'=1,2,3}\left|\sum_m\left(\frac{\tilde{\Xi}_{n'm}{}^{\lambda'}(\hat{q}')\tilde{\Xi}_{m0}{}^{\lambda}(\hat{q})}{\epsilon_m-\epsilon_0-\hbar\omega_{q\lambda}}+\frac{\tilde{\Xi}_{n'm}{}^{\lambda}(\hat{q})\tilde{\Xi}_{m0}{}^{\lambda'}(\hat{q}')}{\epsilon_m-\epsilon_{n'}+\hbar\omega_{q\lambda}}\right)\right|^2. \tag{25}$$

In the familiar limit of $\hbar\omega_{q\lambda} \ll 4\Delta$, $\hbar\omega_{q\lambda} \ll k_BT$ this formula reduces to

$$\alpha_{q\lambda}^{(c)} = \frac{f_0(T)}{4\pi\rho c_\lambda^3}\frac{1}{\hbar k_BT}F^2(q)\sum_{\lambda'}\frac{1}{\rho c_{\lambda'}^5}\left(\frac{4\Delta}{\hbar}\right)^3 n\left(\frac{4\Delta}{\hbar}\right)F^2\left(\frac{4\Delta}{\hbar c_{\lambda'}}\right)$$
$$\times\langle\langle \sum_{n'=1,2,3} |\tilde{\Xi}_{n'0}^{\lambda'}(\hat{q}')\tilde{\Xi}_{00}^{\lambda}(\hat{q}) - \sum_{m=1,2,3} (\tilde{\Xi}_{n'm}^{\lambda}(\hat{q})\tilde{\Xi}_{m0}^{\lambda'}(\hat{q}'))|^2\rangle\rangle. \quad (26)$$

If we compare the expression with Eq. (22) we find that

$$\alpha_{q\lambda}^{(c)} \cong \alpha_{q\lambda}^{(b)}, \quad (27)$$

because the ratio of singlet and triplet state population $f_0(T)/f(T)$ is $\exp(4\Delta/k_BT)$ and $n(4\Delta/\hbar)\exp(4\Delta/k_BT)$ is just $1+n(4\Delta/\hbar)$.

We will conclude this section by applying these results to the experimentally observed acoustic-phonon attenuation. In Figs. (1) and (2) experimental data for the attenuation of transverse phonons at a frequency $\omega = 2\pi\times 9\times 10^9$ sec^{-1} in the temperature range 5 to 40°K in As-doped and P-doped germanium are shown. The theoretical curves are computed qualitatively from the expressions (22) and (26) for $\alpha_{q\lambda}^{(b)}$ and $\alpha_{q\lambda}^{(c)}$ using the appropriate numerical constants given in Sec. II. The contribution from $\alpha_{q\lambda}^{(a)}$ due to elastic scattering is negligible. We see that the agreement between experiment and theory is quite good, in regard to both the magnitude and the temperature dependence of the attenuation. Appreciable deviation is only observed in P-doped germanium for $T \gtrsim 40$°K, where the theoretical calculation predicts a higher attenuation. Qualitatively, this is understandable because in our calculation we have assumed that only the singlet and triplet states are occupied, i.e., $f_0(T)+3f(T)=1$. Thus at high temperature $(T \geq 4\Delta/k_B)$, when the occupation of the higher energy levels is not completely negligible, we are over-estimating $f(T)$ and therefore the attenuation coefficients $\alpha^{(b)}$ and $\alpha^{(c)}$.

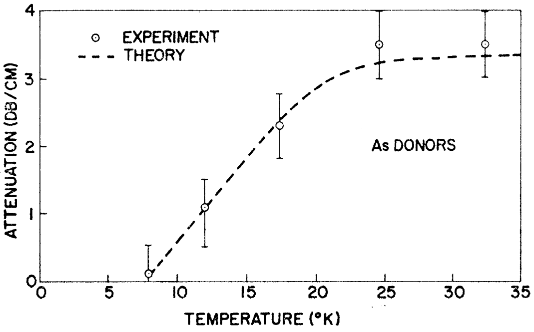

FIG. 1. Attenuation of the transverse wave propagating in the (100) direction of As-doped Ge as a function of temperature. The impurity concentration is 3×10^{15} cm^{-3} and the ultrasonic frequency is $\omega = 2\pi\times 9\times 10^9$ sec^{-1}.

IV. CALCULATION OF RESONANCE ATTENUATION BY THERMODYNAMIC GREEN'S-FUNCTION METHOD

We will now study the phonon attenuation at frequencies such that the perturbation calculation is not valid. If we examine Eqs. (15), (20), and (25) we see immediately that terms in the second-order matrix elements will become infinite when $\hbar\omega_{q\lambda}$ approaches 4Δ or 0. This will also be true for higher order matrix elements. In fact they will approach infinity faster than the second-order terms. Clearly, to get a correct description of the attenuation at such frequencies one must use another method of calculation. The method we shall use is the thermodynamic Green's-function technique. This method is described thoroughly in many places,[15,16] and we shall not go into any detail.

The phonon Green's function is defined as[17]

$$D_{\lambda\lambda'}(\mathbf{q}, \tau_1-\tau_2) = -(\tfrac{1}{4}\omega_{q\lambda}\omega_{q'\lambda'})^{1/2}$$
$$\times\langle T_\tau([a_{q\lambda}(\tau_1)+a_{-q\lambda}^\dagger(\tau_1)]$$
$$\times[a_{q'\lambda'}(\tau_2)+a_{-q'\lambda'}(\tau_2)])\rangle, \quad (28)$$

where the "time" τ is defined in terms of the imaginary time t by

$$t = -i\tau \quad (29)$$

and t is restricted to the interval 0 to $-i/k_BT$, so that τ runs from 0 to $\beta = 1/k_BT$. T_τ denotes a positive-time

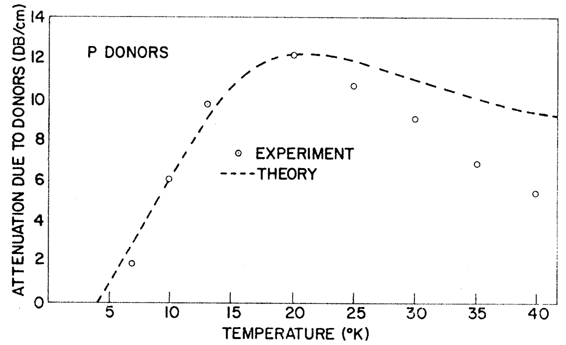

FIG. 2. Attenuation of the same transverse wave in P-doped Ge as a function of temperature. The impurity concentration and ultrasonic frequency are the same as in Fig. 1.

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[15] A. A. Abrikosov, L. P. Gorkov, and I. E. Dzyaloshinski, *Methods of Quantum Field Theory in Statistical Physics* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).

[16] L. P. Kadanoff and G. Baym, *Quantum Statistical Physics* (W. A. Benjamin, Inc., New York, 1962).

[17] We shall follow the notation of Ref. 15.

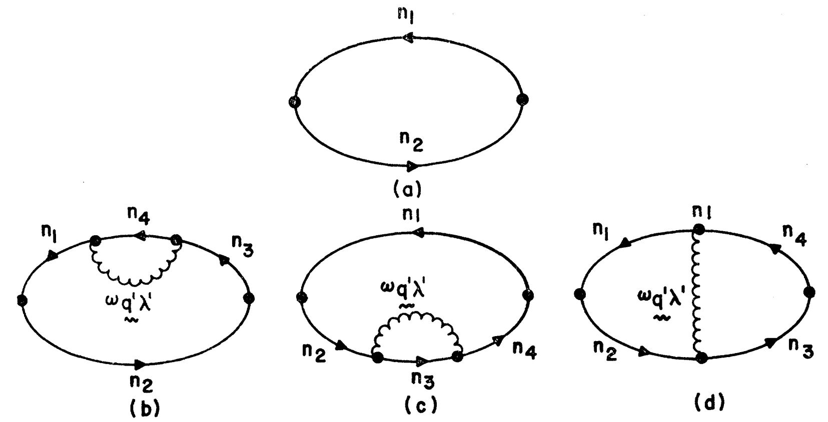

FIG. 3. Phonon self-energy part $\Pi_{\lambda\lambda}(\mathbf{q},\omega_n)$ in perturbation theory: first Born approximation (diagram a); second Born approximation (diagrams b, c, and d). Solid lines represent the noninteracting-electron Green's functions $G_{nn}^{(0)}(\Omega)$. Wavy lines represent the harmonic-phonon Green's functions $D_{\lambda'\lambda'}^{(0)}(\mathbf{q}',\omega')$. The dots represent the bare electron-phonon interaction vertex $\Xi_{nn'}^{\lambda}/(\rho c_\lambda^2)^{1/2}$.

ordering with respect to this interval for τ and $\langle\ \rangle$ denotes the thermal average. The Fourier transform of the phonon Green's function is

$$D_{\lambda\lambda'}(\mathbf{q},\omega_n)=\int_0^\beta d\tau D_{\lambda\lambda'}(\mathbf{q},\tau)e^{i\omega_n\tau}, \tag{30}$$

where

$$\omega_n=2\pi n/\beta,\quad n=\text{integer}.$$

In the noninteracting phonon system, $D_{\lambda\lambda'}(\mathbf{q},\omega_n)$ is given by

$$D_{\lambda\lambda'}^{(0)}(\mathbf{q},\omega_n)=-\delta_{\lambda\lambda'}\omega_{\mathbf{q}\lambda}^2/(\omega_n^2+\omega_{\mathbf{q}\lambda}^2) \tag{31a}$$

or

$$D_{\lambda\lambda'}^{(0)^{-1}}(\mathbf{q},\omega_n)=-\delta_{\lambda\lambda'}(\omega_n^2+\omega_{\mathbf{q}\lambda}^3)/\omega_{\mathbf{q}\lambda}^2. \tag{31b}$$

In the presence of interaction we have the Dyson's equation for D^{-1}

$$D_{\lambda\lambda'}^{-1}(\mathbf{q},\omega_n)=D_{\lambda\lambda'}^{(0)^{-1}}(\mathbf{q},\omega_n)-\Pi_{\lambda\lambda'}(\mathbf{q},\omega_n), \tag{32}$$

where Π is known as the phonon self-energy function. The rules for calculating Π by diagrammatic techniques are given in detail in Ref. 15 in the case of electron-phonon interaction. The change in frequency $\Delta\omega_{\mathbf{q}\lambda}$ and the damping $\gamma_{\mathbf{q}\lambda}$ of the phonon $(\mathbf{q},\lambda)$ due to interaction, are obtained from the self-energy function according to

$$\Delta\omega_{\mathbf{q}\lambda}=\tfrac{1}{2}\omega_{\mathbf{q}\lambda}\lim_{\epsilon\to0^+}\operatorname{Re}\Pi_{\lambda\lambda}(\mathbf{q},\,\omega_n\to-i\omega_{\mathbf{q}\lambda}+\epsilon), \tag{33}$$

$$\gamma_{\mathbf{q}\lambda}=-\tfrac{1}{2}\omega_{\mathbf{q}\lambda}\lim_{\epsilon\to0^+}\operatorname{Im}\Pi_{\lambda\lambda}(\mathbf{q},\,\omega_n\to-i\omega_{\mathbf{q}\lambda}+\epsilon). \tag{34}$$

The attenuation coefficient $\alpha_{\mathbf{q}\lambda}$ is given by

$$\alpha_{\mathbf{q}\lambda}=(1/c_{\mathbf{q}\lambda})\gamma_{\mathbf{q}\lambda}. \tag{35}$$

Similarly, the electron Green's function is defined as

$$G_{nn'}(\tau_1-\tau_2)=-\langle T_\tau[c_n(\tau_1)c_{n'}^\dagger(\tau_2)]\rangle \tag{36}$$

and the Fourier transform $G_{nn'}(\Omega_r)$ as

$$G_{nn'}(\Omega_r)=\int_0^\beta d\tau e^{i\Omega_r\tau}G_{nn'}(\tau) \tag{37}$$

$$\Omega_r=\pi(2r+1)/\beta,\quad r=\text{integer}.$$

For free electrons the Green's function is

$$G_{nn'}^{(0)}(\Omega_r)=\delta_{nn'}/(i\Omega_r-\epsilon_n), \tag{37}$$

or

$$G_{nn'}^{(0)^{-1}}(\Omega_r)=\delta_{nn'}(i\Omega_r-\epsilon_n). \tag{38}$$

In the interacting system the Dyson equation is

$$G_{nn'}^{-1}(\Omega_r)=G_{nn'}^{(0)^{-1}}(\Omega_r)-\Sigma_{nn'}(\Omega_r), \tag{39}$$

where Σ is the electron self-energy part. The level shift and level width of nondegenerate states are obtained from it according to

$$\Delta\epsilon_n=\lim_{\epsilon\to0^+}\operatorname{Re}\Sigma_{nn}(\Omega_r\to-i\epsilon_n+\epsilon) \tag{40}$$

$$\Gamma_n=-\lim_{\epsilon\to0^+}\operatorname{Im}\Sigma_{nn}(\Omega_r\to-i\epsilon_n+\epsilon). \tag{41}$$

For degenerate states the prescription is much more complicated. One has to solve the matrix equation (39) for the set of degenerate states under consideration to determine the correct linear combinations of these states forming the new ones and their energy splittings and widths. For our purpose we shall simply ignore such complications. We shall assume that $G_{nn'}(\Omega_r)$ is also diagonal and apply Eqs. (40) and (41) to the triplet states.

The attenuation coefficients which were previously calculated in the second Born approximation can be obtained by using the Green's-function technique from Eqs. (34) and (35) and the phonon self-energy part Π calculated to fourth order in the electron-phonon cou-

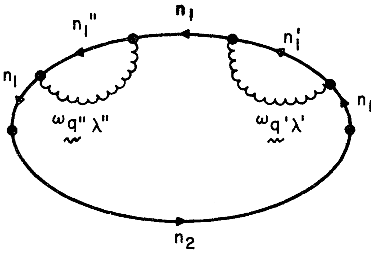

FIG. 4. A higher order phonon self-energy part belonging to the class of diagrams referred to as propagator-correction diagrams.

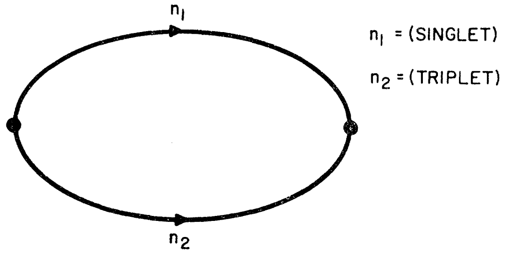

FIG. 5. Phonon self-energy part that contains all propagator corrections (for n_1 = singlet state and n_2 = triplet states). Heavy solid lines represent electron Green's functions $G_{nn}=G_{nn}^{(0)}+G_{nn}^{(0)}\Sigma_{nn}G_{nn}$. Σ_{nn} is electron self-energy part.

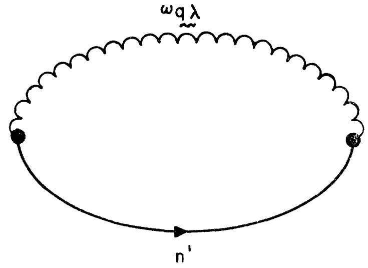

FIG. 6. Electron self-energy part Σ_{nn} in first Born approximation. Notation is same as in Fig. 3.

pling Ξ. The relevant diagrams for Π of this order are shown in diagrams (b), (c), and (d) of Fig. (3). (The phonon-self energy in the first Born approximation is shown in diagram (a) of the same figure.) Diagrams (b) with $n_3=n_1$, and (c) with $n_4=n_2$ are referred to as propagator-correction diagrams, and diagram (d) as a vertex-correction diagram.

Let us now turn our attention to the two situations when the perturbation calculation fails. We will first consider the case when $\hbar\omega_{q\lambda}$ approaches 4Δ. Then we find that the contributions from (b), (c), and (d) become large. However, the largest contributions are easily seen to come from (b) in which $n_3=n_1$= singlet state, n_2= triplet state, and from (c) in which n_1= singlet state, $n_4=n_2$= triplet state. These terms are proportional to $(4\Delta-\hbar\omega_{q\lambda})^{-2}$ while the remaining ones are proportional to $|4\Delta-\hbar\omega_{q\lambda}|^{-1}$. Similarly, in the higher order diagrams for Π, the terms that are proportional to the highest power of $|4\Delta-\hbar\omega_{q\lambda}|^{-1}$ come from propagator-correction terms. One such term is shown in Fig. 4. Therefore we will only keep these terms. Summing all these terms up we obtain Fig. (5) for Π. The heavy solid lines now represent the electron Green's functions in the presence of the electron-phonon interaction. We will use the spectral representation[18] for the electron Green's function $G_{nn}(\Omega)=G_n(\Omega)$

$$G_n(\Omega)=\int_{-\infty}^{\infty}\frac{d\nu}{\pi}\frac{A_n(\nu)}{i\Omega-\nu}, \tag{42}$$

where $A_n(\nu)$ is the spectral function. In the free-electron system it is simply

$$A_n^{(0)}(\nu)=\pi\delta(\nu-\epsilon_n). \tag{43}$$

According to Eq. (41), $A_n(\nu)$ can be obtained from $G_n(\Omega)$ by

$$A_n(\nu)=-\lim_{\epsilon\to 0^+}\operatorname{Im}G_n(\Omega\to -i\nu+\epsilon). \tag{44}$$

Therefore, upon using Eq. (39), we get

$$A_n(\nu)=\Gamma_n(\nu)/[(\nu-\epsilon_n-\Delta\epsilon_n(\nu))^2+\Gamma_n^2(\nu)], \tag{45}$$

where

$$\Gamma_n(\nu)=-\lim_{\epsilon\to 0^+}\operatorname{Im}\Sigma_{nn}(\Omega\to -i\nu+\epsilon), \tag{46}$$

$$\Delta\epsilon_n(\nu)=\lim_{\epsilon\to 0^+}\operatorname{Re}\Sigma_{nn}(\Omega\to -i\nu+\epsilon). \tag{47}$$

To the lowest order in the electron-phonon coupling $\Sigma_{nn}(\Omega)$ is given by Fig. (6), from which we obtain

$$\Delta\epsilon_n(\nu)=\sum_\lambda\sum_m\int d^3q\,|\Xi_{nm}^\lambda(\hat{q})|^2F^2(q)\hbar\omega_{q\lambda}/2\rho c_\lambda^2\{(1+n_{q\lambda})\mathcal{P}(\nu-\hbar\omega_{q\lambda}-\epsilon_m)^{-1}+n_{q\lambda}\mathcal{P}(\nu+\hbar\omega_{q\lambda}-\epsilon_m)^{-1}\} \tag{48}$$

and

$$\begin{aligned}\Gamma_n(\nu)&=\pi\sum_\lambda\sum_m\int d^3q\,|\Xi_{nm}^\lambda(\hat{q})|^2F^2(q)\frac{\hbar\omega_{q\lambda}}{2\rho c_\lambda^2}\{(1+n_{q\lambda})\delta(\nu-\hbar\omega_{q\lambda}-\epsilon_m)+n_{q\lambda}\delta(\nu+\hbar\omega_{q\lambda}-\epsilon_m)\}\\&=\frac{1}{4\pi}\sum_\lambda\sum_m\left\{\frac{1}{\rho c_\lambda^5}\left(\frac{\epsilon_m-\nu}{\hbar}\right)^3F^2\left(\frac{\epsilon_m-\nu}{\hbar}\right)\langle\langle|\Xi_{nm}^\lambda(\hat{q})|^2\rangle\rangle n\left(\frac{\epsilon_m-\nu}{\hbar}\right)\Theta(\epsilon_m-\nu)\right.\\&\qquad\left.+\frac{1}{\rho c_\lambda^5}\left(\frac{\nu-\epsilon_m}{\hbar}\right)^3F^2\left(\frac{\nu-\epsilon_m}{\hbar}\right)\langle\langle|\Xi_{nm}^\lambda(\hat{q})|^2\rangle\rangle\left[1+n\left(\frac{\nu-\epsilon_m}{\hbar}\right)\right]\Theta(\nu-\epsilon_m)\right\},\end{aligned} \tag{49}$$

where Θ is the step function

$$\begin{aligned}\Theta(x)&=0\quad x>0\\&=1\quad x<0.\end{aligned} \tag{50}$$

The level shifts $\Delta\epsilon_n$ and width Γ_n[19] are obtained from

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[18] The spectral representations of Green's functions is described in Refs. 15 and 16.

[19] The level widths for the triplet states have been calculated by Griffin and Carruthers (Ref. 3).

Eqs. (48) and (49) by putting $\nu=\epsilon_n$

$$\begin{aligned}\Delta\epsilon_n&=\Delta\epsilon_n(\nu=\epsilon_n)\\ \Gamma_n&=\Gamma_n(\nu=\epsilon_n).\end{aligned}\tag{51}$$

We can now calculate the phonon-attenuation coefficient from Fig. (5) by using Eqs. (34) and (35) in terms of the spectral function. The result is

$$\alpha_{q\lambda}{}^{(r)}=\frac{\omega_{q\lambda}}{\rho c_\lambda{}^3}(1-e^{-(\hbar\omega_{q\lambda}/k_BT)})F^2(q)\sum_{n=1,2,3}|\tilde{\Xi}_{n0}{}^{\lambda}(\hat{q})|^2 \times\int_{-\infty}^{\infty}\frac{d\nu}{\pi}A_0(\nu)A_n(\nu+\hbar\omega_{q\lambda})f_\nu(T),\tag{52}$$

where $f_\nu(T)$ is Boltzman function

$$f_\nu(T)=Ae^{-(\nu/k_BT)}.\tag{53}$$

Since the width Γ_0 is much less than 4Δ, $A_0(\nu)$ is sharply peaked at $\nu=\epsilon_0$ and we may replace $f_\nu(T)$ by $f_0(T)$ obtaining

$$\alpha_{q\lambda}{}^{(r)}=\frac{\omega_{q\lambda}}{\rho c_\lambda{}^3}(1-e^{-(\hbar\omega_{q\lambda}/k_BT)})f_0(T)F^2(q)\sum_{n=1,2,3}|\tilde{\Xi}_{n0}{}^{\lambda}(\hat{q})|^2 \times\int_{-\infty}^{\infty}\frac{d\nu}{\pi}A_0(\nu)A_n(\nu+\hbar\omega_{q\lambda}).\tag{54}$$

Before we study this expression near resonance, let us observe that by expanding the spectral function in powers of the electron-phonon coupling in the following manner:

$$A_m(\nu)=\pi\delta(\nu-\epsilon_m)+\Gamma_m(\nu)/(\nu-\epsilon_m)^2+\cdots,\tag{55}$$

we get the attenuation coefficient in the first Born approximation (which is zero) and part of the attenuation coefficient in the second Born approximation previously obtained. Near resonance we cannot make such expansion because the resulting energy denominators are small. However, the frequency integral cannot be done unless some simplifying approximation is made on the spectral functions. An obvious choice is to approximate the spectral function by a Lorentzian form. That is, we replace $\Gamma_n(\nu)$ and $\Delta\epsilon_n(\nu)$ in Eq. (45) by Γ_n and $\Delta\epsilon$, obtaining

$$A_n{}^{(l)}(\nu)=\Gamma_n/[(\nu-E_n)^2+\Gamma_n{}^2]\tag{56}$$

$$E_n=\epsilon_n+\Delta\epsilon_n,\tag{57}$$

where E_n is the energy of the nth level in the presence of interaction. Then we can perform the integration and find

$$\alpha_{q\lambda}{}^{(r)}=\frac{\omega_{q\lambda}}{\rho c_\lambda{}^3}(1-e^{-(\hbar\omega_{q\lambda}/k_BT)})f_0(T)F^2(q) \times\sum_{n=1,2,3}|\tilde{\Xi}_{n0}{}^{\lambda}(\hat{q})|^2\frac{\Gamma_0+\Gamma_n}{(4\Delta-\hbar\omega_{q\lambda})^2+(\Gamma_0+\Gamma_n)^2}.\tag{58}$$

In obtaining this expression we have neglected for simplicity the splitting of the triplet states compared to 4Δ and terms that are smaller by Γ_n/ϵ_n. $\alpha_{q\lambda}{}^{(r)}$ is the dominant term in the phonon attenuation when

$$|4\Delta-\hbar\omega_{q\lambda}|<\Gamma_0+\Gamma_n,\quad n=1,2,3,\tag{59}$$

giving[20]

$$\alpha_{q\lambda}{}^{(r)}\cong(\omega_{q\lambda}/\rho c_\lambda{}^3)(1-e^{-(\hbar\omega_{q\lambda}/k_BT)})f_0(T)F^2(q) \times\sum_{n=1,2,3}|\tilde{\Xi}_{n0}{}^{\lambda}(\hat{q})|^2(\Gamma_0+\Gamma_n)^{-1}.\tag{60}$$

On the other hand, when the frequency is off resonance, i.e., $|4\Delta-\hbar\omega_{q\lambda}|>(\Gamma_0+\Gamma_n)$, we obtain

$$\alpha_{q\lambda}{}^{(r)}\cong(\omega_{q\lambda}/\rho c_\lambda{}^3)(1-e^{-(\hbar\omega_{q\lambda}/k_BT)})f_0(T)F^2(q) \times\sum_{n=1,2,3}|\tilde{\Xi}_{n0}{}^{\lambda}(\hat{q})|^2(\Gamma_0+\Gamma_n)/(4\Delta-\hbar\omega_{q\lambda})^2.\tag{61}$$

This extrapolation formula reproduces part of the second Born-approximation results reliably only when $\hbar\omega_{q\lambda}$ is still close to 4Δ, because of the Lorentzian approximation made on the spectral function.

Finally, let us consider the case of very small frequencies. When the frequency $\omega_{q\lambda}$ is smaller than the widths and the energy splittings of the triplet levels we can have the type of processes described by Eq. (13). The attenuation coefficient can be calculated from diagrams similar to Fig. 5, but with $n_1=n_2=$ (singlet) and n_1, $n_2=$ (triplet)

$$\alpha_{q\lambda}=\frac{\omega_{q\lambda}}{\rho c_\lambda{}^3}\frac{\hbar\omega_{q\lambda}}{k_BT}f_0(T)F^2(q)|\tilde{\Xi}_{00}{}^{\lambda}(\hat{q})|^2\frac{2\Gamma_0}{(\hbar\omega_{q\lambda})^2+(2\Gamma_0)^2} +\frac{\omega_{q\lambda}}{\rho c_\lambda{}^3}\frac{\hbar\omega_{q\lambda}}{k_BT}f(T)F^2(q)\sum_{n,n'=1,2,3}|\tilde{\Xi}_{nn'}{}^{\lambda}(\hat{q})|^2 \times\frac{\Gamma_n+\Gamma_{n'}}{(\hbar\omega_{q\lambda}-E_{nn'})^2+(\Gamma_n+\Gamma_{n'})^2}\tag{62}$$

$$E_{nn'}=E_n=E_{n'}=\Delta\epsilon_n-\Delta\epsilon_{n'},\tag{63}$$

where we have assumed that $\hbar\omega_{q\lambda}\ll k_BT$ and used the Lorentzian approximation for the spectral function. $E_{nn'}$ are the energy splittings of the triplet levels by the thermal phonons and are of the order as the widths Γ_n. This expression reduces to the following when $\hbar\omega_{q\lambda}\ll\Gamma_n$:

$$\alpha_{q\lambda}\cong\frac{f_0(T)}{\rho c_\lambda{}^3}\frac{\hbar(\omega_{q\lambda})^2}{k_BT}F^2(q)|\tilde{\Xi}_{00}{}^{\lambda}(\hat{q})|^2\frac{1}{2\Gamma_0}+\frac{f(T)}{\rho c_\lambda{}^3}\frac{\hbar(\omega_{q\lambda})^2}{k_BT}F^2(q) \times\sum_{n,n'=1,2,3}|\tilde{\Xi}_{nn'}{}^{\lambda}(\hat{q})|^2\frac{\Gamma_n+\Gamma_{n'}}{(E_{nn'})^2+(\Gamma_n+\Gamma_{n'})^2}.\tag{64}$$

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[20] This expression for the attenuation coefficient at resonance differs from that obtained by Griffin and Carruthers (Ref. 3).

In fact, formula (62) can be used to describe qualitatively the acoustic attenuation for the entire frequency range[21] $\hbar\omega_{q\lambda}<4\Delta$.

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[21] A phenomenological formula for the total acoustic attenuation coefficient of the form

$$\alpha_\omega=\frac{2}{3}\frac{N_3}{\rho c^3}\frac{\Xi^2}{k_BT}\frac{\omega^2\tau}{1+\omega^2\tau^2}$$

has been derived by M. Pomerantz (Ref. 1). N_3 is the number of impurity atoms per unit volume in the triplet states and τ is a relaxation time to be adjusted to fit the experimental data. One sees immediately that this expression is similar to the second term in Eq. (62) (multiplied by N_i, the impurity concentration) if τ is identified with the life time of a triplet state $(\Gamma/\hbar)^{-1}$. The above formula is no longer valid when $\hbar\omega$ is close to 4Δ.

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Theory of the Third-Order Elastic Constants of Diamond-Like Crystals

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A calculation of the third-order elastic constants of silicon, germanium, and other diamond-like crystals is presented which is based on a previously published method of setting up a suitable form for the elastic strain energy of a crystal. The six third-order constants are calculated in terms of three anharmonic first- and second-neighbor force constants and the two previously determined harmonic force constants. The experimental values of the six coefficients are well fitted by the theoretical expressions involving these three anharmonic force constants. The valence-electron interactions are discussed in the light of the values deduced for these force constants.

I. INTRODUCTION

In a previous article,[1] hereafter referred to as I, the problem of writing down a form for the elastic strain energy of a crystal which exhibits the necessary invariance properties was considered. It was shown that one can write such a strain energy as a function of various scalar products between the vectors representing the relative positions of the nuclei. This method is basically equivalent to the Born-Huang method[2] of imposing the invariance requirements but the physical significance of the different contributions is now more apparent. In this present article, we shall use this form for the anharmonic strain energy as a starting point for a calculation of the third-order elasticity coefficients of crystals of the diamond type. Such a calculation can shed considerable light on the nature of the interatomic interactions in the solid state.

Interest in the third-order elasticity of crystalline solids has arisen only fairly recently and the number of solids for which measurements have been made is still small. The present experimental method[3–7] is to measure the changes in ultrasonic velocity (and thus in the effective elastic constants) under various types of applied static stress. At this time, measurements on silicon,[3,4] germanium,[3,5,7] quartz,[6] sodium chloride,[7] magnesium oxide,[7] and fused SiO_2[7] have been published. Formal theoretical treatments of third-order elasticity based on the Born-Huang formalism have been given by Leibfried and Ludwig[8] and Srinivasan[9] and a few calculations of third-order elasticity of certain primitive cubic crystals have been published.[10] The present work is based on the alternative formalism presented in I which has several advantages over the Born-Huang approach, especially when anharmonicity is included. Availability of experimental data is, of course, one reason why the diamond type of crystal was chosen for the present calculation. The other reasons are (a) that the results of previous work[1,11,12] suggest that only first- and second-neighbor

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