

the second moment of the exciton. The three points shown in Fig. 2 were measured at 300, 440, and 600°K, respectively. Comparing with Martienssen's measurements of the width of the exciton peak as a function of temperature, we find $\langle E_{\text{NC}}^2 \rangle \simeq \langle E_C^2 \rangle$. This is very close to the corresponding result for F centers.

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Soft-Mode Damping and Ultrasonic Attenuation at a Structural Phase Transition

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The soft-mode damping and the ultrasonic attenuation at a displacive phase transition has been calculated with the help of a model Hamiltonian. The soft-mode damping parameter Γ is finite at the transition temperature, whereas the ultrasonic attenuation α is singular. For sound frequencies $\omega \ll \Gamma$, the ultrasonic attenuation is proportional to the sound frequency squared with critical exponents $\eta = 0.5$ and 1.5 , respectively, for weakly damped and strongly overdamped soft-mode frequencies. A comparison is made with previous calculations based on the Silvermann model.

I. INTRODUCTION

A MODEL Hamiltonian has recently been constructed to describe displacive structural phase transitions in perovskite-type crystals of the form ABO_3 involving rotations of the BO_6 octahedra.^{1,2} The model Hamiltonian is expressed in terms of localized displacement fields $\mathbf{R}(l)$ associated with each unit cell where $\mathbf{R}(l)$ is an axial vector describing the rotations of the oxygen octahedra about the cell center.

From the model Hamiltonian, the behavior of the soft dynamical modes associated with the phase transition and the static angular displacement have been calculated as functions of temperature.²

The displacements of the oxygen octahedra are coupled to the static strains.^{3,4} This interaction is important in determining both the amount of distortion and the form of the eigenfrequencies of the coupled system.^{3,4}

In this paper, we present the results for the attenuation of the acoustic phonons and the soft optical phonons due to their mutual interaction. A model Hamiltonian may be constructed by expanding the potential energy of the strained crystal in terms of the strain and the oxygen-ion displacement fields. Then, making use of the transformation given in Ref. 2 connecting the oxygen-ion displacements and the operators $\mathbf{R}(l)$, the

Hamiltonian takes the form⁵

$$H = \sum G_{\alpha\beta ij\lambda\lambda'} [e_{\alpha\beta}(l) + e_{\alpha\beta}(l')] \gamma_{ij}(ll') \times [R_\lambda(l)R_{\lambda'}(l') + R_\lambda(l')R_{\lambda'}(l)], \quad (1)$$

where $e_{ij}(l)$ are localized strain tensor components. There are four independent coupling constants $G_{\alpha\beta ij\lambda\lambda'}$, and these are listed in the Appendix. The coupling function $\gamma_{ij}(ll')$ is a symmetric matrix. When expressed in terms of its Fourier transform,

$$\gamma_{ij}(ll') = (1/N) \sum_{\mathbf{q}} e^{i\mathbf{q} \cdot [\mathbf{x}(l) - \mathbf{x}(l')]} \gamma_{ij}(\mathbf{q}), \quad (2)$$

it has the simple form

$$\begin{aligned} \gamma_{ij}(\mathbf{q}) &= \frac{1}{2}(1 - \cos q_i a) \quad \text{for } i = j, \\ \gamma_{ij}(\mathbf{q}) &= \frac{1}{2}(1 - \cos q_k a) \quad \text{for } i \neq j \neq k, \end{aligned} \quad (3)$$

where i, j , and k refer to the three Cartesian coordinates. The vector $\mathbf{X}(l)$ denotes the center of the l th unit cell.

Because

$$\gamma_{ij}(q=0) = 0, \quad (4)$$

the Hamiltonian vanishes when all the octahedra rotate in phase as required on physical grounds. We also note that

$$\gamma_{ij}(\mathbf{q}_R) = 1 \quad (5)$$

for all i and j , where \mathbf{q}_R is the wave vector at the R corner of the Brillouin zone.

The Hamiltonian Eq. (1) has the proper symmetry and transformation properties appropriate for the cubic

⁵ A more detailed derivation of the model Hamiltonian will be presented in Ref. 4.

¹ H. Thomas and K. A. Müller, Phys. Rev. Letters **21**, 1256 (1968).

² E. Pytte and J. Feder, Phys. Rev. **187**, 1077 (1969).

³ J. C. Slonczewski and H. Thomas (to be published).

⁴ J. Feder and E. Pytte (to be published).

perovskite structure. The distortion from cubic symmetry below the transition temperature is described by nonvanishing expectation values of the operators $R_\lambda(l)$, and the strains $e_{ij}(l)$. The strain tensor $e_{ij}(l)$ will, however, have nonvanishing expectation values also in the cubic phase above the transition temperature which then describes the usual thermal expansion. We set²

$$R_\lambda(l) = \langle R_\lambda(l) \rangle + r_\lambda(l), \quad (6)$$

where the angular brackets denote the thermal average and $r_\lambda(l)$ describes the fluctuation about this average value. As the direction of the displacement alternates from one cell to the next, we write

$$\langle R_\lambda(l) \rangle = A_\lambda e^{i\mathbf{q}_R \cdot \mathbf{x}(l)}. \quad (7)$$

For the strain tensor, we set

$$e_{ij}(l) = \langle e_{ij}(l) \rangle + u_{ij}(l). \quad (8)$$

The fluctuations about the average values of the strain may be expressed in terms of the normal-mode coordinates of the acoustic phonons in the usual way,

$$u_{ij}(l) = \frac{1}{2}i(1/\sqrt{N}) \sum_{\mu\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{x}(l)} [q_i e_j(\mu\mathbf{q}) + q_j e_i(\mu\mathbf{q})] Q(\mu\mathbf{q}), \quad (9)$$

where $Q(\mu\mathbf{q})$ is the normal-mode coordinate for the μ th

acoustic branch of frequency $\omega(\mu\mathbf{q})$, wave vector \mathbf{q} , and polarization vector $\mathbf{e}(\mu\mathbf{q})$.

For $r_\lambda(l)$ we make use of the expansion

$$r_\lambda(l) = (1/\sqrt{N}) \sum_{\lambda'\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{x}(l)} b_{\lambda\lambda'}(\mathbf{q}) s_{\lambda'}(\mathbf{q}), \quad (10)$$

with $b_{\lambda\lambda'}(\mathbf{q})$ and $s_\lambda(\mathbf{q})$ as defined in Ref. 2.

When the Hamiltonian Eq. (1) is expressed in terms of the static and dynamic parts of $R_\lambda(l)$ and $e_{ij}(l)$ by means of Eqs. (6) and (8), the Hamiltonian will consist of (1) static terms depending only on the expectation values $\langle e_{ij}(l) \rangle$ and $\langle R_\lambda(l) \rangle$, (2) terms linear in the normal-mode coordinate $r_\lambda(l)$, (3) terms linear in $u_{ij}(l)$, (4) terms containing products of $u_{ij}(l)$ and $r_\lambda(l)$, and (5) terms bilinear in the operators $r_\lambda(l)$ and linear in $u_{ij}(l)$.

The contribution of the first four sets of terms to the static properties of the system and to the soft-optical-mode frequencies is discussed elsewhere.⁴ (These terms do not affect the acoustic-mode frequencies.) In this paper, terms 4 and 5 will be considered. For simplicity, the discussion will be restricted to the case of tetragonal distortion. Then, only one of the components A_λ is different from zero,⁶

$$A_\lambda = A \delta_{\lambda 3}. \quad (11)$$

The resonant interaction Hamiltonian then takes the form

$$\begin{aligned} H_R = A \sum_{ll'} e^{i\mathbf{q}_R \cdot \mathbf{x}(l)} & \left(\frac{1}{2} G_{11} [u_{33}(l) + u_{33}(l')] [\gamma_{11}(ll') + \gamma_{22}(ll')] \right. \\ & + G_{12} \{ [u_{11}(l) + u_{11}(l')] \gamma_{22}(ll') + [u_{22}(l) + u_{22}(l')] \gamma_{11}(ll') \} + G_{13} \{ [u_{11}(l) + u_{11}(l')] [\gamma_{11}(ll') - \gamma_{22}(ll')] \\ & + [u_{22}(l) + u_{22}(l')] [\gamma_{22}(ll') - \gamma_{11}(ll')] \} r_3(l') + 2G_{44} A \sum_{ll'} e^{i\mathbf{q}_R \cdot \mathbf{x}(l)} \{ [u_{13}(l) + u_{13}(l')] \gamma_{13}(ll') r_1(l') \\ & \left. + [u_{23}(l) + u_{23}(l')] \gamma_{23}(ll') r_2(l') \} \right). \quad (12) \end{aligned}$$

Making use of the expansions of $u_{ij}(l)$ and $r_\lambda(l)$ in terms of the normal-mode coordinates Eqs. (9) and (10), this Hamiltonian may be written

$$H_R = iA \sum_{\lambda\mu\mathbf{q}} f_\lambda(\mu\mathbf{q}) Q(\mu\mathbf{q}) s_\lambda(\mathbf{q}_R - \mathbf{q}), \quad (13)$$

where the form of the coupling factors $f_\lambda(\mu\mathbf{q})$ follows trivially from Eqs. (3), (9), and (10). The resonant interaction is proportional to A and is therefore different from zero only in the distorted phase.

Similarly, the scattering terms which have the same form as Eq. (1), with $R_\lambda(l)$ and $e_{ij}(l)$ replaced by $r_\lambda(l)$ and $u_{ij}(l)$, may be written in the form

$$H_S = \sum_{\mathbf{k}\mathbf{q}, \lambda\lambda'\mu} h_{\lambda\lambda'}(\mu\mathbf{k}\mathbf{q}) Q(\mu\mathbf{q}) s_\lambda(-\mathbf{k}) s_{\lambda'}(\mathbf{k} - \mathbf{q}). \quad (14)$$

In the subsequent calculations it will be convenient

⁶ Whereas in Refs. 2 and 4 it was convenient to use the 1 axis as c axis, in this paper the more conventional notation with the 3 axis as c axis will be used.

to make use of the Green's functions

$$\begin{aligned} D_\mu(\mathbf{q}, t-t') &= -i \langle [Q_\mu(\mathbf{q}t) Q_\mu(-\mathbf{q}t')]_+ \rangle, \\ G_\lambda(\mathbf{q}, t-t') &= -i \langle [s_\lambda(\mathbf{q}t) s_\lambda(-\mathbf{q}t')]_+ \rangle, \end{aligned} \quad (15)$$

where the $+$ denotes the Wick time-ordering operation. In the case of commuting operators $[A(t), B(t)] = 0$, the equations of motion for the Green's function $G(t-t') = -i \langle [A(t) B(t')]_+ \rangle$ may be written

$$\begin{aligned} -(\partial^2/\partial t^2) G(t-t') &= i\delta(t-t') \langle [(\partial/\partial t) A(t), B(t)] \rangle \\ &+ (-i) \langle [-(\partial^2/\partial t^2) A(t) B(t')]_+ \rangle. \end{aligned} \quad (16)$$

These Green's functions possess Fourier series expansions and spectral representations⁷

$$G(t-t') = \frac{1}{(-i\beta)} \sum_\nu e^{-i\omega_\nu(t-t')} G(\omega_\nu), \quad (17)$$

$$G(\omega_\nu) = \int \frac{d\omega}{2\pi} \frac{A(\omega)}{\omega_\nu - \omega}, \quad (18)$$

⁷ See, e.g., L. P. Kadanoff and G. Baym, *Quantum Statistical Mechanics* (W. A. Benjamin, Inc., New York, 1962).

with $\omega_\nu = \pi\nu/(-i\beta)$ where ν is an even integer. For the acoustic phonons, we have

$$(\partial/\partial t)Q(\mu\mathbf{q}) = (1/M)P(\mu, -\mathbf{q}), \quad (19)$$

where M is the mass of the unit cell and $P(\mu\mathbf{q})$ is the canonical conjugate momentum to the normal-mode coordinate $Q(\mu\mathbf{q})$,

$$[Q_\mu(\mathbf{q}), P_{\mu'}(\mathbf{q}')] = i\delta_{\mu\mu'}\delta_{\mathbf{q}\mathbf{q}'}. \quad (20)$$

For the optical-phonon modes,² we have

$$(\partial/\partial t)s_\lambda(\mathbf{q}) = p_\lambda(-\mathbf{q}), \quad (21)$$

where

$$[s_\lambda(\mathbf{q}), p_{\lambda'}(\mathbf{q}')] = i\delta_{\lambda\lambda'}\delta_{\mathbf{q}\mathbf{q}'}. \quad (22)$$

The contribution of the scattering interaction H_S to the soft-mode attenuation and to the ultrasonic attenuation will be considered in Secs. II and III, respectively, and in Sec. IV the effect of the resonant interaction H_R will be discussed.

II. SOFT-MODE DAMPING

In the presence of the scattering interaction, the equations of motion for the optical-phonon Green's functions take the form

$$\begin{aligned} & -(\partial^2/\partial t^2)G_\lambda(\mathbf{k}, t-t') - \epsilon_\lambda^2(\mathbf{k})G_\lambda(\mathbf{k}, t-t') \\ & = \delta(t-t') - i \sum_{\lambda'\mu\mathbf{q}} g_{\lambda\lambda'}(\mu\mathbf{k}\mathbf{q}) \\ & \times \langle (s_{\lambda'}(\mathbf{k}-\mathbf{q}, t)Q(\mu\mathbf{q}t)s_\lambda(-\mathbf{k}t'))_+ \rangle, \end{aligned} \quad (23)$$

where

$$g_{\lambda\lambda'}(\mu\mathbf{k}\mathbf{q}) = h_{\lambda\lambda'}(\mu\mathbf{k}\mathbf{q}) + h_{\lambda'\lambda}(\mu, \mathbf{q}-\mathbf{k}, \mathbf{q}). \quad (24)$$

The left-hand side and the first term on the right-hand side represent the result for noninteracting optical phonons.² In the last term which is due to the coupling to the acoustic phonons, we make a perturbation expansion⁸ and keep only the lowest-order terms which are proportional to the coupling constants squared. The interaction term may then be expressed in terms of products of acoustic- and optical-phonon Green's functions. Making use of the Fourier series expansion Eq. (17), we obtain

$$[\omega_\nu^2 - \epsilon_\lambda^2(\mathbf{k}) - \Sigma_\lambda(\mathbf{k}\omega_\nu)]G_\lambda(\mathbf{k}\omega_\nu) = 1, \quad (25)$$

$$\begin{aligned} \Gamma_\lambda^o(\mathbf{k}\omega) = & \frac{\pi}{16M} \sum_{\lambda'\mu\mathbf{q}} \frac{g_{\lambda\lambda'}(\mu\mathbf{k}\mathbf{q})g_{\lambda\lambda'}(\mu, -\mathbf{k}, -\mathbf{q})}{\omega(\mu\mathbf{q})} \left(\frac{1}{\omega+\omega(\mu\mathbf{q})} \frac{1}{\omega} \{ \coth \frac{1}{2}\beta\omega(\mu\mathbf{q}) - \coth \frac{1}{2}\beta[\omega+\omega(\mu\mathbf{q})] \} \right. \\ & \times \delta(\omega - \epsilon_{\lambda'}(\mathbf{k}-\mathbf{q}) + \omega(\mu\mathbf{q})) + \frac{1}{\omega - \omega(\mu\mathbf{q})} \frac{1}{\omega} \{ \coth \frac{1}{2}\beta\omega(\mu\mathbf{q}) + \coth \frac{1}{2}\beta[\omega - \omega(\mu\mathbf{q})] \} \\ & \left. \times \delta(\omega + \epsilon_{\lambda'}(\mathbf{k}-\mathbf{q}) - \omega(\mu\mathbf{q})) \right). \end{aligned} \quad (32)$$

⁸ See, e.g., H. S. Bennett and E. Pytte, Phys. Rev. **155**, 553 (1967), Appendix A.

where

$$\begin{aligned} \Sigma_\lambda(\mathbf{k}\omega_\nu) = & i \sum_{\lambda'\mu\mathbf{q}} g_{\lambda\lambda'}(\mu\mathbf{k}\mathbf{q})g_{\lambda\lambda'}(\mu, -\mathbf{k}, -\mathbf{q}) \\ & \times \frac{1}{(-i\beta)} \sum_{\nu'} G_{\lambda'}(\mathbf{k}-\mathbf{q}, \omega_\nu - \omega_{\nu'}) D_\mu(\mathbf{q}, \omega_{\nu'}). \end{aligned} \quad (26)$$

Further, using the spectral representation Eq. (18) for the Green's function and the summation formula

$$\frac{1}{\beta} \sum_{\nu'} \frac{1}{\omega_\nu - \epsilon} = -\frac{1}{2} \coth \frac{1}{2}\beta\epsilon, \quad (27)$$

the expression for Σ_λ may be written

$$\begin{aligned} \Sigma_\lambda(\mathbf{k}z) = & \frac{1}{2} \sum_{\lambda'\mu\mathbf{q}} g_{\lambda\lambda'}(\mu\mathbf{k}\mathbf{q})g_{\lambda\lambda'}(\mu, -\mathbf{k}, -\mathbf{q}) \\ & \int \frac{d\omega d\omega'}{(2\pi)^2} (\coth \frac{1}{2}\beta\omega - \coth \frac{1}{2}\beta\omega') \\ & \times \frac{A_{\lambda'}^o(\mathbf{k}-\mathbf{q}, \omega)A_{\mu}^a(\mathbf{q}, \omega')}{z + \omega' - \omega}, \end{aligned} \quad (28)$$

where the superscripts are used to distinguish the spectral weight functions of the acoustic- and optical-phonon Green's functions.

The function $\Sigma_\lambda(\mathbf{k}z)$ is an analytic function of the complex variable z except on the real axis. When we approach the real axis from above, we may define the real and imaginary parts of Σ_λ by the relation

$$\lim_{\epsilon \rightarrow 0} \Sigma_\lambda(\mathbf{k}, \omega + i\epsilon) = \text{Re}\Sigma_\lambda(\mathbf{k}\omega) - i \text{Im}\Sigma_\lambda(\mathbf{k}\omega). \quad (29)$$

The real part of Σ_λ will give a shift in the optical-phonon frequencies ϵ_λ , while the imaginary part will give an attenuation. In $\Sigma_\lambda(\mathbf{k}\omega)$, we substitute the spectral weight functions for noninteracting optical and acoustic phonons,

$$\begin{aligned} A_{\mu}^a(\mathbf{q}\omega) = & [\pi/M\omega(\mu\mathbf{q})][\delta(\omega - \omega(\mu\mathbf{q})) - \delta(\omega + \omega(\mu\mathbf{q}))], \\ A_{\lambda}^o(\mathbf{q}\omega) = & [\pi/\epsilon_\lambda(\mathbf{q})][\delta(\omega - \epsilon_\lambda(\mathbf{q})) - \delta(\omega + \epsilon_\lambda(\mathbf{q}))]. \end{aligned} \quad (30)$$

From Eq. (28) the imaginary part may then be written

$$\text{Im}\Sigma_\lambda(\mathbf{k}\omega) = 2\omega\Gamma_\lambda^o(\mathbf{k}\omega), \quad (31)$$

where

In order to calculate the damping of the soft mode at the R corner of the Brillouin zone, we evaluate $\Gamma_{\lambda}^o(\mathbf{k}\omega)$ for $\omega = \epsilon_{\lambda}(\mathbf{k})$ and $\mathbf{k} = \mathbf{q}_R$. If we assume that the optical-phonon spectrum is isotropic in the neighborhood of $\mathbf{q} = \mathbf{q}_R$, it may be written in the form²

$$\epsilon_{\lambda}^2(\mathbf{q}_R - \mathbf{q}) = \epsilon_{\lambda}^2(T) + \alpha_{\lambda}^2 q^2, \quad (33)$$

where

$$\epsilon_{\lambda}(T) \xrightarrow{T \rightarrow T_a} a_{\lambda}(|T - T_a|)^{1/2}, \quad (34)$$

with a_{λ} in general different for $T > T_a$ and $T < T_a$. The mode $\epsilon_3(T)$ is a singlet, whereas $\epsilon_1(T) = \epsilon_2(T)$ is doubly degenerate. For the acoustic-phonon frequencies, we use the linear approximation

$$\omega(\mu\mathbf{q}) = c_{\mu}q. \quad (35)$$

The integrals in Eq. (32) will be evaluated in the limit $T \rightarrow T_a$. Because of the energy-conserving δ functions, only relatively small values of q will contribute, which justifies the use of the small q form of the spectra. For $T < T_a$, we obtain

$$\begin{aligned} \Gamma_{1,2}^o &= (a^3/15\pi)(1/M\beta_a) \\ &\quad \times \{(3G_{11}^2 + 8G_{12}^2 + 4G_{11}G_{12} + 4G_{44}^2)I_{11}(l) \\ &\quad + 4G_{44}^2I_{13}(l) + 2G_{44}^2[I_{13}(l) + I_{11}(l)]\}, \quad (36) \\ \Gamma_3^o &= (a^3/15\pi)(1/M\beta_a)\{(3G_{11}^2 + 8G_{12}^2 + 4G_{11}G_{12}) \\ &\quad \times I_{33}(l) + 8G_{44}^2I_{13}(l) + 4G_{44}^2I_{13}(l)\}, \end{aligned}$$

where $I_{\lambda\lambda'}(\mu)$ is given by

$$I_{\lambda\lambda'}(\mu) = \frac{1}{4c_{\mu}^2} \left(\frac{Q_+^2}{|\epsilon_{\lambda'} + c_{\mu}Q_+| |c_{\mu}\epsilon_{\lambda'} - (\alpha_{\lambda}^2 - c_{\mu}^2)Q_+|} + \frac{Q_-^2}{|\epsilon_{\lambda'} + c_{\mu}Q_-| |c_{\mu}\epsilon_{\lambda'} - (\alpha_{\lambda}^2 - c_{\mu}^2)Q_-|} \right), \quad (37)$$

with

$$Q_{+,-} = [1/(\alpha_{\lambda}^2 - c_{\mu}^2)] \{c_{\mu}\epsilon_{\lambda'} \pm [c_{\mu}^2\epsilon_{\lambda}^2 + \alpha_{\lambda}^2(\epsilon_{\lambda}^2 - \epsilon_{\lambda'}^2)]^{1/2}\}. \quad (38)$$

For $\lambda = \lambda'$ the expression for $I_{\lambda\lambda'}$ has the simple form

$$I_{\lambda\lambda}(\mu) = \frac{1}{c_{\mu}} \frac{1}{|c_{\mu}^4 - \alpha_{\lambda}^4|}. \quad (39)$$

For $T > T_a$, the optical-phonon frequencies are degenerate, under the assumption that the spectra are isotropic, and the expressions for the soft-mode damping given above both reduce to

$$\begin{aligned} \Gamma^o &= \frac{a^3}{15\pi M\beta_a} \left((3G_{11}^2 + 8G_{12}^2 + 4G_{11}G_{12} + 8G_{44}^2) \right. \\ &\quad \times \frac{1}{c_l |c_l^4 - \alpha^4|} + 4G_{44}^2 \frac{1}{c_t |c_t^4 - \alpha^4|} \left. \right), \quad (40) \end{aligned}$$

where c_l and c_t are the sound velocities, respectively,

for longitudinal and transverse acoustic phonons in the undistorted structure.

In this derivation use has been made of Eq. (5) and the fact that²

$$b_{\lambda\lambda'}(\mathbf{q}_R) = \delta_{\lambda\lambda'} \quad (41)$$

in order to simplify the coupling factors. In all cases $\Gamma_{\lambda}^o(T)$ goes to a constant value $\neq 0$ as $T \rightarrow T_a$.⁹

This result should be compared to the singular behavior obtained in a recent calculation of the soft-mode attenuation at a displacive phase transition¹⁰ based on the one-dimensional Silvermann model.¹¹ The singularity is due to the different phase-space factors in the one-dimensional model. If the integral in Eq. (32) is evaluated for the case that all the wave vectors are one-dimensional we obtain a singularity of the form

$$\Gamma^o(T) \xrightarrow{T \rightarrow T_a} \frac{b}{(|T - T_a|)}. \quad (42)$$

III. ULTRASONIC ATTENUATION

The ultrasonic attenuation is obtained analogously from the acoustic-phonon Green's function. For the latter we obtain

$$[\omega_{\nu}^2 - \omega^2(\mu\mathbf{q}) - P_{\mu}(\mathbf{q}\omega_{\nu})]D_{\mu}(\mathbf{q}\omega_{\nu}) = 1/M, \quad (43)$$

where

$$P_{\mu}(\mathbf{q}\omega_{\nu}) = - \frac{i}{M} \frac{1}{-i\beta} \sum_{\mathbf{k}\nu'} g_{\lambda\lambda'}(\mu\mathbf{k}\mathbf{q}) h_{\lambda\lambda'}(\mu, -\mathbf{k}, -\mathbf{q}) \times G_{\lambda'}(\mathbf{k}\omega_{\nu'}) G_{\lambda}(\mathbf{k} - \mathbf{q}, \omega_{\nu'} - \omega_{\nu}) \quad (44)$$

describes the interaction with the optical phonons. Making use of the spectral representation for $G_{\lambda}(k\omega_{\nu})$ and performing the ν' summation gives

$$\begin{aligned} P_{\mu}(\mathbf{q}\omega_{\nu}) &= \frac{1}{2M} \sum_{\lambda\lambda', \mathbf{k}} g_{\lambda\lambda'}(\mu\mathbf{k}\mathbf{q}) h_{\lambda\lambda'}(\mu, -\mathbf{k}, -\mathbf{q}) \\ &\quad \times \int \frac{d\omega d\omega'}{(2\pi)^2} A_{\lambda'}^o(\mathbf{k}\omega) A_{\lambda}^o(\mathbf{k} - \mathbf{q}, \omega') \\ &\quad \times \frac{[\coth \frac{1}{2}\beta\omega - \coth \frac{1}{2}\beta\omega']}{\omega_{\nu} + \omega' - \omega}. \quad (45) \end{aligned}$$

Then defining the real and imaginary parts of $P_{\mu}(\mathbf{q}\omega)$ as in Eq. (29) for $\Sigma_{\lambda}(\mathbf{k}\omega)$, we obtain

$$\begin{aligned} \text{Im} P_{\mu}(\mathbf{q}\omega) &= \frac{1}{4M} \sum_{\lambda\lambda', \mathbf{k}} g_{\lambda\lambda'}(\mu\mathbf{k}\mathbf{q}) h_{\lambda\lambda'}(\mu, -\mathbf{k}, -\mathbf{q}) \\ &\quad \times \int \frac{d\omega'}{2\pi} A_{\lambda'}^o(\mathbf{k}\omega') A_{\lambda}^o(\omega' - \omega, \mathbf{k} - \mathbf{q}) \\ &\quad + [\coth \frac{1}{2}\beta\omega' - \coth \frac{1}{2}\beta(\omega' - \omega)]. \quad (46) \end{aligned}$$

⁹ However, it should be noted that because the calculation is based on perturbation theory, it is, strictly speaking, valid only for $\epsilon_{\lambda} > \Gamma_{\lambda}^o$.

¹⁰ K. Tani, Phys. Letters **25A**, 400 (1967).

¹¹ B. D. Silvermann, Phys. Rev. **125**, 1921 (1962).

Whereas in the calculation of the soft-mode attenuation the damping of the acoustic phonons could be neglected, in the calculation of the ultrasonic attenuation it is important to include the damping of the soft optical-phonon modes. In the frequency and temperature ranges of interest for ultrasonic attenuation experiments, it will usually be true that $\omega_\mu \ll \Gamma_\lambda^0$ even when $\Gamma_\lambda^0 \ll \epsilon_\lambda$ and the soft modes are underdamped.

When the soft-mode damping is included, it follows from Eqs. (18), (25), and (31) that the spectral weight function $A^0(\mathbf{k}\omega)$ may be written

$$A^0(\mathbf{k}\omega) = \frac{4\omega\Gamma_\lambda^0(\mathbf{k}\omega)}{[\omega^2 - \epsilon_\lambda^2(\mathbf{k})]^2 + 4\omega^2\Gamma_\lambda^0(\mathbf{k}\omega)}. \quad (47)$$

In the limit $\Gamma_\lambda^0(\mathbf{k}\omega) \rightarrow 0$, this expression reduces to that for the free optical-phonon Green's function given by Eq. (30).

The ultrasonic attenuation coefficient $\alpha_\mu(\mathbf{q})$ is defined by

$$\omega_\mu(\mathbf{q}) = c_\mu(q - i\alpha_\mu(\mathbf{q})), \quad (48)$$

and is related to $\text{Im}P_\mu(\mathbf{q},\omega)$ by

$$\alpha_\mu(\mathbf{q}) = [1/2\omega_\mu(\mathbf{q})c_\mu] \text{Im}P_\mu(\mathbf{q},\omega_\mu(\mathbf{q})). \quad (49)$$

The expression for $\text{Im}P_\mu(\mathbf{q},\omega)$ has been evaluated for $\omega = \omega_\mu(\mathbf{q})$ in the limit $q \rightarrow 0$ and $T \rightarrow T_a$ for different relative values of ω_μ , ϵ_λ , and Γ_λ^0 . The leading contribution to the summation in Eq. (46) comes from $\mathbf{k} \approx \mathbf{q}_R$, and Eqs. (5) and (41) may again be used to simplify the coupling factors. Explicit expressions for the latter will be given only for sound propagation along the crystal axes.

For $T < T_a$, different results are obtained for propagation along the c axis and along an a axis. For longitudinal phonons the ultrasonic attenuation may be written

$$\begin{aligned} \alpha_l(q) &= B(\omega_l)[G_{11}^2K_{33} + 2G_{12}^2K_{11}], \\ \alpha_t(q) &= B(\omega_t)[G_{11}^2K_{11} + G_{12}^2(K_{33} + K_{11})] \end{aligned} \quad (50)$$

for these two cases, respectively. The form of $B(\omega_\mu)$ and $K_{\lambda\lambda'}$ will be given below. For transverse phonons propagating along the c axis or along an a axis with its polarization vector along the c axis, then

$$\alpha_t(q) = B(\omega_t)2G_{44}^2K_{13} \quad (51)$$

whereas the attenuation for a transverse mode propagating along an a axis with its polarization vector along the other a axis is given by

$$\alpha_t(q) = B(\omega_t)2G_{44}^2K_{11}. \quad (52)$$

For $T > T_a$, α_μ is given by

$$\begin{aligned} \alpha_l(q) &= B(\omega_l)[G_{11}^2 + 2G_{12}^2]K, \\ \alpha_t(q) &= B(\omega_t)2G_{44}^2K, \end{aligned} \quad (53)$$

respectively, for longitudinal and transverse phonons propagating along a cube axis. Because the optical-

phonon modes are degenerate for $T > T_a$, we have dropped the subscripts on K .

For $B(\omega_\mu)$ and $K_{\lambda\lambda'}$, only the leading contributions in the limit $\omega_\mu \rightarrow 0$ and $T \rightarrow T_a$ will be given. For $\Gamma^0(k\omega) \equiv 0$ we obtain, under the assumption that $\omega_\mu \ll \epsilon_\lambda$,

$$B(\omega_\mu) = (a^3/8\pi)(\omega_\mu/M\beta_a c_\mu^2), \quad (54)$$

$$\begin{aligned} K_{\lambda\lambda} &= [(\alpha_\lambda^2 - c_\mu^2)^{1/2}/\alpha_\lambda^4 \epsilon_\lambda], \quad \text{for } \alpha_\lambda > c_\mu \\ K_{\lambda\lambda} &\approx 0, \quad \text{for } \alpha_\lambda < c_\mu. \end{aligned} \quad (55)$$

The coefficients α_λ are defined by Eq. (33). The condition $\alpha_\lambda > c_\mu$ in Eq. (55) is required in order for energy and momentum conservation to be satisfied for the process in which an optical phonon is scattered with the emission or absorption of an acoustic phonon. The off-diagonal component K_{13} will be smaller than $K_{\lambda\lambda}$ by a factor of order ω/ϵ , even when conditions on the relative values of α_λ and c_μ are satisfied, because of the different gaps in the $\epsilon_1(q)$ and $\epsilon_3(q)$ spectra. Thus for $\Gamma_\lambda^0 = 0$ the leading contribution to the ultrasonic attenuation is linear in the sound frequency and has a square root singularity at $T = T_a$,

$$\alpha \propto \omega/(|T - T_a|)^{1/2}, \quad (56)$$

provided a soft-mode frequency exists for which $\alpha_\lambda > c_\mu$.

If we evaluate the expression Eq. (46) for $\Gamma_\lambda^0 = 0$, $\alpha_\lambda > c_\mu$, and for one-dimensional wave-vector dependences, we obtain

$$\alpha \propto \omega/(|T - T_a|)^{3/2}, \quad (57)$$

which agrees with the result obtained by Tani and Tsuda¹² using the Silvermann model. To give a correct description of the soft-mode damping and the ultrasonic attenuation, a generalization of the model to three dimensions is required.

Because $\Gamma_\lambda^0 \ll \omega_\mu$ is usually not an interesting case experimentally, more detailed results for $\Gamma_\lambda^0 = 0$ will not be given. When $\Gamma_\lambda^0 \neq 0$ and $\omega_\mu \ll \Gamma_\lambda^0$, the ultrasonic attenuation will be proportional to the phonon frequency squared. We obtain

$$B(\omega_\mu) = \frac{a^3}{32\pi M\beta_a c_\mu^3} \omega_\mu^2. \quad (58)$$

If the soft modes are underdamped such that $\epsilon_\lambda \gg \Gamma_\lambda^0$, then $K_{\lambda\lambda'}$ is given by

$$K_{\lambda\lambda} = 1/\alpha_\lambda^3 \Gamma_\lambda^0 \epsilon_\lambda, \quad (59)$$

with K_{13} smaller by a factor of the order of Γ^0/ϵ^2 . For overdamped soft modes when $\Gamma_\lambda^0 \gg \epsilon_\lambda$, we obtain

$$\begin{aligned} K_{\lambda\lambda'} &= [16\Gamma_\lambda^0 \Gamma_{\lambda'}^0 \alpha_\lambda \alpha_{\lambda'} / (\alpha_\lambda \epsilon_{\lambda'} + \alpha_{\lambda'} \epsilon_\lambda)] \\ &\quad \times [\alpha_{\lambda'} \epsilon_\lambda (\Gamma_\lambda^0 \alpha_{\lambda'}^2 + \Gamma_{\lambda'}^0 \alpha_\lambda^2)^{1/2} \\ &\quad + \alpha_\lambda \alpha_{\lambda'} (\Gamma_\lambda^0 \epsilon_{\lambda'}^2 + \Gamma_{\lambda'}^0 \epsilon_\lambda^2)^{1/2}]^{-1} \\ &\quad \times [\alpha_\lambda \epsilon_{\lambda'} (\Gamma_\lambda^0 \alpha_{\lambda'}^2 + \Gamma_{\lambda'}^0 \alpha_\lambda^2)^{1/2} \\ &\quad + \alpha_{\lambda'} \epsilon_\lambda (\Gamma_\lambda^0 \epsilon_{\lambda'}^2 + \Gamma_{\lambda'}^0 \epsilon_\lambda^2)^{1/2}]^{-1}. \end{aligned} \quad (60)$$

¹² K. Tani and N. Tsuda, Phys. Letters 25A, 529 (1967).

The diagonal elements of this matrix reduce to the simple form

$$K_{\lambda\lambda} = \Gamma_{\lambda}^{\circ} / \alpha_{\lambda}^3 \epsilon_{\lambda}^3. \quad (61)$$

We obtain a different temperature dependence in the neighborhood of the transition temperature, depending on whether the soft mode is underdamped or overdamped in the temperature region where the ultrasonic attenuation^{*} becomes large. For $\omega_{\mu} \ll \Gamma_{\lambda}^{\circ}$ and $\Gamma_{\lambda}^{\circ} \ll \epsilon_{\lambda}$,

$$\alpha \propto \omega^2 / (|T - T_a|)^{1/2}, \quad (62)$$

whereas

$$\alpha \propto \omega^2 / (|T - T_a|)^{3/2} \quad (63)$$

for $\Gamma_{\lambda}^{\circ} \gg \epsilon_{\lambda}$.

Because the critical scattering of sound occurs very close to the transition temperature, it is to be expected that the soft mode will, in most cases, be overdamped.

IV. RESONANT INTERACTION

The resonant interaction described by Eq. (13) leads to coupled acoustic- and optical-phonon modes. The dispersion equation for the coupled modes may be derived from the equations of motion of either the acoustic- or the optical-phonon Green's function.

For a weakly coupled system, the acoustic-phonon Green's function may be written

$$[z^2 - \omega^2(\mu\mathbf{q}) - P_{\mu}(\mathbf{qz}) + (A^2/M) \sum_{\lambda} f_{\lambda}(\mu\mathbf{q}) f_{\lambda}(\mu, -\mathbf{q}) \times G_{\lambda}(\mathbf{q}_R - \mathbf{q}, z)] D_{\mu}(\mathbf{qz}) = 1/M, \quad (64)$$

where the last term in the bracket is due to the resonant interaction. The contribution of the scattering interaction Eq. (14) to $P_{\mu}(\mathbf{qz})$ was calculated in Sec. III. The poles of the Green's function $D_{\mu}(\mathbf{qz})$ determine the eigenfrequencies. Although the derivation of this expression is based on perturbation theory, we include the attenuations of the acoustic and optical phonons calculated in the preceding sections. Substituting for the optical-phonon Green's function, we obtain the dispersion relation

$$z^2 - \omega^2(\mu\mathbf{q}) + 2iz\Gamma_{\mu}^a(\mathbf{qz}) - \frac{A^2}{M} \times \sum_{\lambda} \frac{f_{\lambda}(\mu\mathbf{q}) f_{\lambda}(\mu, -\mathbf{q})}{z^2 - \epsilon_{\lambda}^2(\mathbf{q}_R - \mathbf{q}) + 2iz\Gamma_{\lambda}^{\circ}(\mathbf{q}_R - \mathbf{q}, z)} = 0. \quad (65)$$

Alternatively from the optical-phonon Green's function, we obtain the complementary expression

$$z^2 - \epsilon_{\lambda}^2(\mathbf{q}_R - \mathbf{q}) - 2iz\Gamma_{\lambda}^{\circ}(\mathbf{q}_R - \mathbf{q}, z) - \frac{A^2}{M} \times \sum_{\mu} \frac{f_{\lambda}(\mu\mathbf{q}) f_{\lambda}(\mu, -\mathbf{q})}{z^2 - \omega^2(\mu\mathbf{q}) + 2iz\Gamma_{\mu}^a(\mathbf{qz})} = 0. \quad (66)$$

The coupling factors $f_{\lambda}(\mu\mathbf{q})$ are proportional to the wave vector q . The resonant interaction will therefore

not affect the optical-phonon frequencies at $\mathbf{q} = \mathbf{q}_R$. It will give a shift in the coefficients α_{λ} of the q^2 term in the dispersion curve Eq. (33) and in the sound velocities of the acoustic modes. Because the coefficients α_{λ} are not well known, even in the absence of the coupling, we consider only the shift in the velocities of the acoustic modes.

If we consider sound propagation only along certain symmetry directions in the small- q limit, a given acoustic mode will couple only to a single optical-phonon mode ϵ_{λ} . The dispersion curves Eqs. (65) and (66) then reduce to

$$[z^2 - \omega^2(\mu\mathbf{q}) + 2iz\Gamma_{\lambda}^a(\mathbf{qz})] \times [z^2 - \epsilon_{\lambda}^2(\mathbf{q}_R - \mathbf{q}) + 2iz\Gamma_{\lambda}^{\circ}(\mathbf{q}_R - \mathbf{q}, z)] = (4A^2/M) q^2 G^2(\mu\lambda), \quad (67)$$

where the coupling constants $G(\mu\lambda)$ may be determined from Eqs. (12) and (13) for the particular cases considered.

In order to study the changes in the sound velocity due to the resonant interaction, we set $z \approx \omega(\mu\mathbf{q})$ and consider the small- q limit. For $\omega_{\mu} \ll \epsilon_{\lambda}$, we obtain from Eq. (67),

$$\tilde{\omega}_{\mu} = \omega_{\mu} \left(1 - \frac{2A^2}{Mc_{\mu}^2} \frac{G^2(\mu\lambda)}{\epsilon_{\lambda}^2} \frac{1}{1 + \omega_{\mu}^2 \tau_{\lambda}^2} \right) - i \left(\Gamma_{\mu}^a + \frac{2A^2}{M} \frac{G^2(\mu\lambda)}{q^2} \frac{\tau_{\lambda}}{\epsilon_{\lambda}^2} \frac{1}{1 + \omega_{\mu}^2 \tau_{\lambda}^2} \right), \quad (68)$$

where

$$\tau_{\lambda}(\mathbf{q}) = 2\Gamma_{\lambda}^{\circ}(\mathbf{q}_R - \mathbf{q}, \omega(\mu\mathbf{q})) / \epsilon_{\lambda}^2(\mathbf{q}_R - \mathbf{q}), \quad (69)$$

$$\Gamma_{\mu}^a(\mathbf{q}) = \Gamma_{\mu}^a(\mathbf{q}, \omega(\mu\mathbf{q})).$$

Similar expressions for the frequency shift and the ultrasonic attenuation have been derived by Zurek¹³ using the Landau-Khalatnikov theory. The relaxation time τ_{λ} is singular provided the soft-mode relaxation frequency $\Gamma_{\lambda}^{\circ}(\mathbf{q}_R - \mathbf{q}, \omega(\mu\mathbf{q}))$ goes to a finite nonzero value in the limit $T \rightarrow T_a$. Then

$$\tau_{\lambda} = \frac{2\Gamma_{\lambda}^{\circ}}{\epsilon_{\lambda}^2} \xrightarrow{T \rightarrow T_a} \frac{d_{\lambda}}{(T_a - T)}. \quad (70)$$

If the soft-mode damping is neglected, a finite discontinuity in the sound velocity is obtained at $T = T_a$, since both A^2 and ϵ_{λ}^2 are proportional to $(T_a - T)$ for $T \lesssim T_a$. The effect of the factor $1/(1 + \omega^2 \tau^2)$ is to smooth out the discontinuity. Because of the frequency dependence of $\Gamma_{\lambda}^{\circ}(\omega)$ the value of Γ_{λ}° in Eq. (70) is not directly related to the soft-mode linewidth.

Making use of the relationship between the sound frequencies and the elastic constants, we may deduce from Eq. (68) the corresponding changes in the fre-

¹³ R. Zurek, thesis, Technische Hochschule München, 1969 (unpublished).

quency-dependent elastic constants. We obtain

$$\begin{aligned}\tilde{c}_{11}(\omega) &= c_{11} - G_{12}^2 D_3(\omega), & \tilde{c}_{33}(\omega) &= c_{11} - G_{11}^2 D_3(\omega), \\ \tilde{c}_{12} &= c_{12} - G_{12}^2 D_3(\omega), & \tilde{c}_{13}(\omega) &= c_{12} - G_{11} G_{12} D_3(\omega), \\ \tilde{c}_{44} &= c_{44} - G_{44}^2 D_1(\omega), & \tilde{c}_{66} &= c_{44}.\end{aligned}\quad (71)$$

Here

$$D_\lambda(\omega) = \frac{4\rho A^2}{M \epsilon_\lambda^2} \frac{1}{1 + \omega^2 \tau_\lambda^2}, \quad (72)$$

where ρ is the density of the crystal. The $\omega=0$ limit of these expressions has also been obtained by Slonczewski and Thomas^{3,14} from a phenomenological energy expression.

In addition to the shift in the sound velocity given by Eq. (68), a singular contribution is obtained from the real part of the function $P(\mathbf{q}, z)$ discussed in Sec. III, of the form

$$B_\mu \omega_\mu^0 / |T - T_a|^{1/2},$$

where B_μ is a constant. This dependence is independent of the relative values of ω , Γ^0 , and ϵ .

From Eq. (68) the contribution of the resonant interaction to the ultrasonic attenuation may be written

$$\alpha_\mu(q) = \frac{4G^2(\mu\lambda)A^2}{Mc_\mu^3} \frac{1}{\epsilon_\lambda^2} \frac{\omega_\mu^2 \tau_\lambda}{1 + \omega_\mu^2 \tau_\lambda^2}. \quad (73)$$

For a longitudinal mode propagating along a crystal axis, then, the coupling constants $G(l3)=G(l2)=0$, while $G(l3)$ is equal to G_{11} for propagation along the c axis, and equal to G_{12} for propagation along an a axis. For a transverse mode propagating along the c axis and along an a axis with its polarization vector along the c axis,

$$\begin{aligned}G(l3) &= 0, & G(l1) &= G_{44} & \text{or} & & G(l1) &= 0, \\ G(l2) &= 0 & \text{or} & & G(l2) &= G_{44}.\end{aligned}\quad (74)$$

A transverse mode propagating along an a axis with its polarization vector along the other a axis does not couple to the optical phonons via the resonant interaction, as may be seen directly from Eq. (12).

¹⁴ However, in Ref. 3 it was assumed that $G_{11} = -2G_{12}$.

The ultrasonic attenuation given by Eq. (73) peaks for $\omega_\mu \tau_\lambda \approx 1$ and then goes to zero as $T \rightarrow T_a$. For temperatures such that $\omega \tau \ll 1$, the attenuation will have the form of an additional singular contribution,

$$\alpha \propto \omega^2 / (T_a - T). \quad (75)$$

V. CONCLUSION

In this paper interactions between soft optical and acoustic phonons have been studied with the help of a model Hamiltonian. Although this Hamiltonian was constructed for phase transitions connected with the condensation of a particular optical-phonon mode in a particular structure, results such as the constant value of Γ at $T = T_a$ and the dependence of the ultrasonic attenuation on ω and the soft-mode frequency ϵ may be expected to apply also to other displacive phase transitions for which the coupling is linear in the strain and bilinear in the soft optical normal-mode coordinates, independent of whether the phonon instability occurs at $q=0$, $\mathbf{q}=\mathbf{q}_R$, or at a general point in the Brillouin zone. It should be emphasized, however, that the critical exponents have been derived only for isotropic spectra, whereas the soft-mode frequencies are in many cases very anisotropic. Furthermore, a linear dependence of ϵ_λ^2 on $|T - T_a|$ has been assumed for $T \approx T_a$. This dependence presumably breaks down sufficiently close to T_a .

APPENDIX

The interaction Hamiltonian Eq. (1) contains four independent constants:

$$\begin{aligned}\frac{1}{4}G_{11} &= G_{112211} = G_{113311} = G_{221122} = G_{223322} \\ &= G_{331133} = G_{332233}, \\ \frac{1}{2}G_{13} &= G_{111122} = G_{111133} = G_{222211} = G_{222233} \\ &= G_{333311} = G_{333322}, \\ \frac{1}{2}(G_{12} - G_{13}) &= G_{112233} = G_{113322} = G_{221133} = G_{223311} \\ &= G_{331122} = G_{332211}, \\ G_{44} &= G_{121212} = G_{131313} = G_{232323}.\end{aligned}$$

All other coupling constants are equal to zero.