[8]S. Geller, Acta Cryst. 10, 243 (1957).
[9]As can be seen from Table II, this is predicted also by linear interpolation between values of lattice constants of the end members.
[10]The $T_t$'s predicted for $PrAlO_3$ and $NdAlO_3$ by J. F. Scott [Phys. Rev. 183, 823 (1969)] are, respectively, 320 and 380 K too low.
[11]J. S. Ruiz, A. Anthony, and M. Foëx, Compt. Rend. 264, 1271 (1967).
[12]V. N. Pavlikov, L. M. Lopato, and S. G. Tresvyatskii, Izv. Akad. Nauk SSSR Neorgan. Materialy 2, 679 (1966).

PHYSICAL REVIEW B VOLUME 2, NUMBER 4 15 AUGUST 1970

# Two-Phonon Resonances and Hybridization of the Resonance with Single-Phonon States*

J. Ruvalds and A. Zawadowski†
*Department of Physics, University of Virginia, Charlottesville, Virginia* 22903
(Received 14 January 1970)

Considering the anharmonic phonon-phonon interactions, two-phonon resonances are studied by Green's-function methods. The two-phonon spectrum exhibits an asymmetric peak near the top of the two-phonon continuum. In the special case of a resonance consisting of two acoustic phonons, the hybridization of the resonance with a single optical phonon is possible, in agreement with experiment.

It has recently been proposed[1] that the anharmonic phonon-phonon interaction can give rise to two-phonon bound states which explain the anomalous peak observed in the second-order Raman spectrum of diamond.[2,3]

The purpose of the present work is to show that phonon-phonon interactions can have a striking influence on the *first-order* as well as the second-order spectrum. First we show that the second-order spectrum is modified in an essential way by the formation of two-phonon resonances under quite general conditions, in contrast to the case of two-phonon bound states which can occur only for a limited range of anharmonic coupling. Furthermore, we demonstrate that the first-order spectrum may exhibit structure as a result of hybridization of a two-phonon resonance with single-phonon states.

We wish to relate our results to Raman scattering experiments and therefore consider only resonances with total momentum $\vec{K}=0$.[4] In the case of resonances consisting of optic-mode phonons the momenta of the individual phonons $\vec{k}_1$ and $\vec{k}_2$ obey the relation $\vec{k}_1=-\vec{k}_2\cong 0$. For resonances of acoustic phonons, the individual phonons have wave vectors $\vec{k}_1=-\vec{k}_2=\vec{\kappa}^i$, where the $\vec{\kappa}^i$ $(i=1,2,\ldots)$ refer to equivalent edges of the Brillouin zone. In both cases the resonance is formed from states near the top of the phonon band.

The Hamiltonian including third- and fourth-order anharmonic terms can be written as $\mathcal{H}=\mathcal{H}_{\text{harmonic}}+\mathcal{H}_3+\mathcal{H}_4$, where $\mathcal{H}_{\text{harmonic}}$ is the usual phonon Hamiltonian in the harmonic approximation. The third-order term $\mathcal{H}_3$ will contribute to the finite lifetime of the single-phonon excitations. We include these broadening effects for the single-phonon states by means of a phenomenological width $\Gamma$, which will be considered as a constant in the energy range of interest.

Since the phonon energies of interest are much greater than the thermal energies considered experimentally, we employ the Green's-function formalism for zero temperature. The effects of finite temperature can then be included in the phenomenological parameters which enter into the calculation.

Following the usual notation,[5] we introduce a propagator for a single phonon

$$D_1(\vec{k},\omega)=\tfrac{1}{2}\omega(\vec{k})\left(\{\omega-[\omega(\vec{k})-\tfrac{1}{2}i\Gamma]\}^{-1}\right.$$
$$\left.-\{\omega+[\omega(\vec{k})-\tfrac{1}{2}i\Gamma]\}^{-1}\right), \qquad (1)$$

where $\omega(\vec{k})$ is the single-phonon energy and $\Gamma$ is a phenomenological width against decay into other phonons, for example, the decay of a single optic phonon into two acoustic phonons. The above Green's function is the Fourier transform of the usual Green's function in the coordinate representation $D_1(x,x')=-i\langle T[\phi(x)\phi(x')]\rangle$, where $T$ denotes the time-ordering operator and the phonon field amplitudes[5] $\phi(x)$ are given by

$$\phi(x) = (1/V^{1/2}) \sum_{\vec{k}} [\omega(\vec{k})/2]^{1/2} \times (b_{\vec{k}} e^{i(\vec{k}\cdot\vec{x} - \omega(\vec{k})t)} + b_{\vec{k}}^{\dagger} e^{-i(\vec{k}\cdot\vec{x} - \omega(\vec{k})t)}) \ . \quad (2)$$

In Eq. (2) the crystal volume is denoted by $V$ and the phonon creation and destruction operators are designated by $b_{\vec{k}}^{\dagger}$ and $b_{\vec{k}}$, respectively. In terms of the $\phi$ amplitudes, a model Hamiltonian for two interacting phonons can be written in the following form[6]:

$$\mathcal{H} = \sum_{\vec{k}} \omega(\vec{k}) [b_{\vec{k}}^{\dagger} b_{\vec{k}} + \tfrac{1}{2}] + (g_4/4!V) \int \phi(x)\phi(x)\phi(x)\phi(x)\, d^3x \ . \quad (3)$$

To investigate the nature of the two-phonon states including anharmonic terms we consider the Bethe-Salpeter equation for the two-phonon Green's function

$$D_2(x, x') = -i \langle T\{\phi(x)\phi(x)\phi(x')\phi(x')\}\rangle \ ,$$

which is related to the strength of the Raman scattering. The Bethe-Salpeter equation corresponds to the summation of the diagrams shown in Fig. 1(a), and is given by[7]

$$D_2(x, x') = i\{2[D_1(x, x')]^2 + ig_4 \int [D(x, x_1) D(x_1, x')]^2 dx, + (ig_4)^2 \cdots\} \ . \quad (4)$$

The solution of Eq. (4) for the case of total momentum $\vec{K} = 0$ is given by

$$D_2(\vec{K} = 0, \omega) = 2F(\omega)/[1 - \tfrac{1}{2} g_4 F(\omega)] \ , \quad (5)$$

where $F(\omega)$ is defined as

$$F(\omega) = [i/(2\pi)^4] \int d^3k \int d\tilde{\omega}\, D_1(\vec{k}, \omega - \tilde{\omega})\, D_1(-\vec{k}, \tilde{\omega}) \ . \quad (6)$$

In order to evaluate the integrals in Eq. (6), we assume a parabolic dispersion law for the phonons near the top of the phonon band. The corresponding one-phonon density of states can be then written in the simple form

$$\rho_1(\omega) = \alpha(\omega_0 - \omega)^{1/2} = \alpha(\omega')^{1/2} \quad \text{for } \omega' > 0, \quad (7)$$

where $\omega_0$ is the maximum single-phonon energy and $\omega' \equiv \omega_0 - \omega$. In addition, we introduce a cutoff energy $\Delta$ which corresponds to the single-phonon bandwidth. Making use of Eqs. (1) and (7) we obtain the $F(\omega)$ defined by Eq. (6) in the form of a simple integral:

$$F(\omega) = \tfrac{1}{4}\omega_0^2 \alpha \int_0^{\Delta} d\omega' (\omega')^{1/2} \times \frac{1}{\omega - 2(\omega_0 - \omega') + i\Gamma} = 2\lambda f(\epsilon, \gamma) \ , \quad (8)$$

where $\lambda = \frac{1}{8}\alpha\omega_0^2\Delta^{1/2}$, $\epsilon = (\omega - 2\omega_0)/\Delta$, $\gamma = \Gamma/\Delta$, and the dimensionless quantity $f$ can be obtained by numerical methods. In Eq. (8) we have restricted our region of interest to energies near $2\omega_0$ and consequently consider only the first terms of the phonon propagator defined in Eq. (1) and subsequently, in the amplitude of the phonon propagator, we make the replacement $\omega(\vec{k}) \cong \omega_0$. Finally, making use of Eqs. (5) and (8), the two-phonon propagator becomes

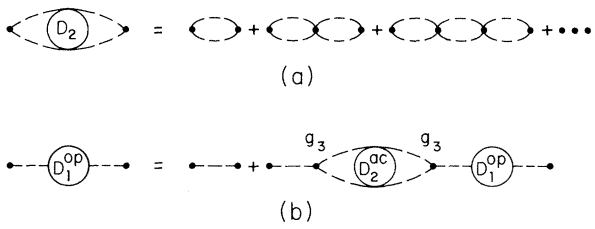


FIG. 1. (a) Bethe-Salpeter equation for the two-phonon propagator $D_2$; (b) Dyson equation for $D_1^{op}$ in diagrammatic representation.

$$D_2(\vec{K} = 0, \omega) = (4\lambda/g_4')f[1/g_4' - f]^{-1} \ , \quad (9)$$

where the dimensionless anharmonic coupling constant is $g_4' \equiv \lambda g_4$.

The two-phonon spectrum $\rho_2$ is related to the propagator in Eq. (9) by

$$\rho_2(\vec{K} = 0, \omega) = -1/(\pi\omega_0^2)\, \mathrm{Im} D_2(\vec{K} = 0, \omega) \ , \quad (10)$$

where the factor $\omega_0^{-2}$ arises from the use of the phonon field operators in the definition of the Green's function. In the limit $g_4' = 0$, one obtains the spectral density for two noninteracting phonons as $\rho_2^{(0)} = (\alpha/4)(\omega_0 - \omega/2)^{1/2}$, for $\omega \leq 2\omega_0$; and $\rho_2^{(0)} = 0$ for $\omega > 2\omega_0$. For the limiting case of $\Gamma = 0$, i.e., phonon states having infinite lifetime, the function $f$ can be calculated analytically for all values of the coupling $g_4'$; such a calculation[8] shows that for $g_4' \leq 1$, a two-phonon resonance exists and the width of the peak corresponding to the resonance becomes quite narrow as $g_4'$ approaches unity. For values $g_4' > 1$ a two-phonon bound state is formed.[1,8] In the present paper we consider phonons with a small but finite width $\Gamma$, and arbitrary values of $g_4'$.

First we consider two-phonon resonances (i.e., $g_4' \leq 1$) and calculate the two-phonon spectrum numerically using Eqs. (8)–(10). The results of this calculation are presented in Fig. 2. In the figure it is apparent that as $g_4'$ approaches, but remains less than unity, the spectrum exhibits a sharp peak corresponding to a two-phonon resonance. As the value of the anharmonicity decreases, the peak, which is superimposed on the continuum spectrum (dotted line), shifts in the direction of decreasing energy and broadens substantially. Finally, as the anharmonic strength $g_4'$ tends to zero, the spectrum reduces to the noninteracting-phonon density of states $\rho_2^{(0)}$ in agree-

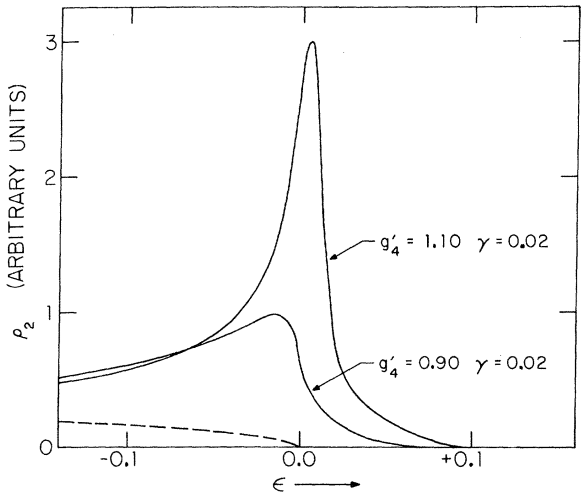


FIG. 2. Spectral function $\rho_2$ plotted as a function of energy for different values of the anharmonic coupling constant $g_4'$. Solid curve for $g_4' = 1.1$ shows a peak corresponding to a two-phonon bound state and the $g_4' = 0.9$ line exhibits structure related to a resonance. For comparison the dotted line shows the phonon density of states in the absence of phonon-phonon interactions.

ment with the analytic limit discussed previously.

If the anharmonicity is sufficiently large (i.e., $g_4' > 1$), a two-phonon bound state splits off the top of the two-phonon continuum and a sharp peak appears in $\rho_2(\vec{K} = 0, \omega)$ at an energy higher than twice the maximum single-phonon energy in accord with the results of Ref. 1. In the event that the single-phonon width $\Gamma$ is much less than the separation in energy of the peak from the top of the continuum, the peak will be quite symmetric. However, as the width becomes comparable in magnitude to the above energy separation, the peak corresponding to the bound state becomes very asymmetric as shown in Fig. 2. It is gratifying to note that the shape of the bound-state peak in Fig. 2 bears a striking resemblance to the line shape of the anomalous peak which has been observed in the two-phonon Raman spectrum of diamond.[2,3]

Recent experimental results for the Raman spectrum of various crystals have exhibited interference effects between one- and two-phonon excitations.[9] Using the theoretical approach discussed above we can interpret these interference effects in terms of the hybridization of single-phonon states with a two-phonon resonance or bound state, as the case may be. In particular, the two-phonon resonance with total momentum $\vec{K} = 0$ could be formed from two acoustic phonons near the top of the acoustic spectrum and in special cases (i.e., for certain temperatures) the resonance energy can coincide with the energy of a single optic-mode phonon whose momentum is $\vec{k} = \vec{K}$. The hybridization is caused by the third-order anharmonic terms in the Hamiltonian which induce transitions from acoustic two-phonon states to a single optic phonon.

In terms of our model Hamiltonian, the third-order anharmonic terms can be expressed in the form

$$\mathcal{H}_3 = (g_3/V^{1/2}) \int \phi^{ac}(x)\phi^{ac}(x)\phi^{op}(x)\, d^3x \quad , \qquad (11)$$

where the superscripts "ac" and "op" designate phonon field operators corresponding to acoustic and optic modes, respectively, and $g_3$ is the third-order coupling constant. To illustrate the formation of the hybrid states we consider the Green's function for an optic phonon;

$$D_1^{op}(x, x') = -i\langle T\{\phi^{op}(x)\phi^{op}(x')\}\rangle \quad . \qquad (12)$$

The third-order anharmonic terms in the Hamiltonian are responsible for the main contribution to the single-phonon lifetime discussed previously. Thus we can write the Dyson equation in terms of the Green's function $D_1^{(0)\,op}(x, x')$ defined by Eq. (1), with the $\omega(\vec{k})$ replaced by the optical-phonon energy $\omega^{op}$ taken at $\vec{k} = 0$, and the width $\Gamma = 0$. Broadening of the single optic phonon due to the $\mathcal{H}_3$ term will henceforth be taken into account explicitly.

Turning now to the acoustic-phonon resonance we use the results of Eqs. (1)–(10).[10] Thus we obtain the Dyson equation shown in diagramatic form in Fig. 1(b), which has the formal solution in the momentum representation

$$D_1^{op}(\vec{k}, \omega) = \frac{D_1^{(0)\,op}(\vec{k}, \omega)}{1 - g_3^2 D_1^{(0)\,op}(\vec{k}, \omega) D_2^{(0)\,ac}(\vec{K} \simeq \vec{k}, \omega)} \quad . \qquad (13)$$

In Eq. (13) we again restrict our attention to energies near the resonance energy and use $\omega \sim \omega^{op} \sim 2\omega_0^{ac}$, and then include for $D_1^{(0)\,op}$ only the leading term in Eq. (1). Furthermore, we use the propagator defined in Eq. (9) for $D_2^{(0)\,ac}$. As in the derivation of Eq. (10), the spectrum for the single optic phonon becomes

$$\rho_1^{op}(\vec{K} = 0, \omega) = -2(\pi\omega_0^{op})\, \mathrm{Im}\, D_1^{op} = -(1/\pi) \times \mathrm{Im}\left[\frac{1}{\omega - \omega_0^{op}[1 + (g_3')^2(g_4')^{-1} f(1/g_4' - f)^{-1}]}\right],$$

where we used Eqs. (1), (9), (13), and defined a dimensionless coupling constant $(g_3')^2 = 2\lambda g_3^2$.

The spectrum $\rho_1^{op}$ is plotted as a function of energy in Fig. 3, and exhibits in some cases two peaks corresponding to (a) the optic phonon and the two-acoustic-phonon resonance, respectively, if they are well separated in energy, and (b) to the

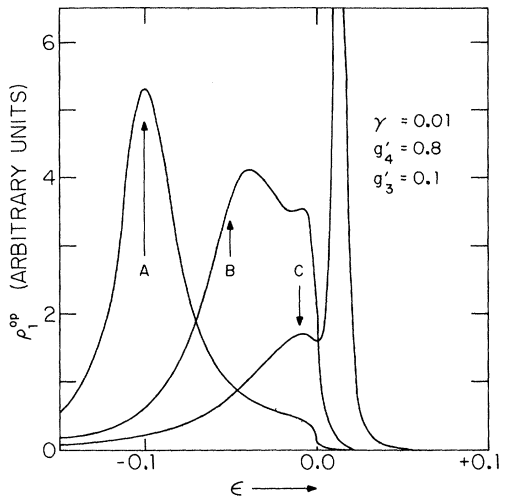


FIG. 3. Illustration of the hybridization of a two-acoustic-phonon resonance with a single-optic-mode phonon. Spectrum $\rho_1^{op}$ is shown as a function of energy for various values of the renormalized ($g_3'=0$) optic phonon energy $\omega_0^{op}$. Arrows indicate the position of $\epsilon_0 = (\omega_0^{op} - 2\omega_0^{ac})/\Delta$; $\epsilon_A = -0.10$, $\epsilon_B = -0.05$, and $\epsilon_C = -0.01$.

shifted energies of the mixed state (hybrid) in the case of strong coupling. One can see in Fig. 3 that as $\omega^{op}$ moves to the top of the acoustic-phonon continuum the corresponding peak becomes quite narrow; thus the optic phonon is less likely to decay into two acoustic phonons since the density of final states $\rho_2^{(0)\,ac}$ decreases. When the renormalized optic energy is above the continuum, the excitation becomes stabilized against decay and exhibits an extremely sharp peak [Fig. 3(c)]. In the resonance region the hybrid peak corresponding to the resonance is strongly deformed as in Fig. 3(b). It is worth noting that the optic peak is usually shifted more than the resonance. Calculated curves of $\rho_1^{op}$ for various values of $g_3'$ show that the relative intensities of the above peaks are determined by $g_3'$ as follows: (a) for $g_3' \ll 0.2$, the optic mode dominates the spectrum; (b) for $g_3' \simeq 0.2$, the two peaks have approximately the same weight; (c) for $g_3' \gg 0.2$ (i.e., large-coupling limit), the optic peak disappears.

The spectrum $\rho_1^{op}$ would show up in first-order Raman scattering; thus the appearance and behavior of the double peaks observed in Scott's[10] experiments on quartz are compatible with the present theory. Neutron scattering experiments should also be able to resolve the structure in $\rho_1^{op}$.

In the second-order Raman spectrum the structure due to the renormalized $\rho_2^{ac}$ would appear as well and would exhibit peaks at somewhat shifted energies. Hybridization of phonon states in the above manner thus suggests the existence of an interference term between first- and second-order processes which is superimposed on the first- and second-order Raman spectra.

The present formalism can readily be extended to treat several phonon branches as well. In this case structure in the phonon dispersion relations could result in additional structure in the spectrum.

It is a pleasure to acknowledge stimulating discussions with Professor V. Celli, Professor M. H. Cohen, and Dr. J. Scott.

---

*Research supported in part by the Center for Advanced Studies at the University of Virginia, Charlottesville, Va. 22903.

†Permanent address: Central Research Institute for Physics, Budapest, Hungary.

[1]M. H. Cohen and J. Ruvalds, Phys. Rev. Letters 23, 1378 (1969).

[2]R. S. Krishnan, Proc. Indian Acad. Sci. 24, 25 (1946).

[3]S. Solin and A. K. Ramdas, Phys. Rev. B 1, 1687 (1970).

[4]Resonances with small total momentum $K \sim 0$ also exist and can be treated by an extension of the present work.

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

[6]Formally, the general expression for the phonon-phonon interaction is given as [see, for example, G. Leibfried and W. Ludwig, Solid State Phys. 12, 276 (1961)]

$$\mathcal{H}_4 = \tfrac{1}{4!}(1/N)\sum \Phi^{\vec{k}_1\vec{k}_2\vec{k}_3\vec{k}_4}_{S_1S_2S_3S_4}\, a^{*}_{\vec{k}_1 s_1}\, a^{*}_{\vec{k}_2 s_2}\, a_{\vec{k}_3 s_3}\, a_{\vec{k}_4 s_4}\,,$$

where the summation is over $\vec{k}_1\vec{k}_2\vec{k}_3\vec{k}_4 S_1S_2S_3S_4$, and where the $a_{\vec{k}s}$'s are related in a simple manner to the phonon operators $a_{\vec{k}s} = [\hbar/2\omega_s(\vec{k})]^{1/2}(b^{\dagger}_{\vec{k}s} + b_{\vec{k}s})$. Near the top of the two-phonon continuum, in a small region of the Brillouin zone, it is a reasonable approximation to write the Hamiltonian in the form shown in Eq. (4) and neglect the $k$ dependence of the anharmonic coupling coefficient $g_4$. This coefficient can be related to the crystal force constants implicit in $\Phi$ by straightforward substitution of the field operators $\phi(x)$ into Eq. (4) to obtain the corresponding expression for $\mathcal{H}_4$. For the sake of simplicity we consider only a single branch of the phonon spectrum.

[7]The factor of 2 in Eq. (6) is due to the possible pairings of the field operators $\phi(x)$.

[8]M. H. Cohen, J. Ruvalds, and A. Zawadowski (unpublished).

[9]See, for example, J. F. Scott, Phys. Rev. Letters 21, 907 (1968), and references cited therein.

[10]The effect of the $\mathcal{H}_3$ terms on $D_2^{ac}$ is to change the coupling constant $g_4$. This contribution is proportional to $g_3^2$ and can be included by the renormalization of $g_4$.