INDIRECT COUPLING AND ANTIRESONANCE OF TWO OPTIC PHONONS*

A. Zawadowski† and J. Ruvalds
Department of Physics, University of Virginia, Charlottesville, Virginia 22903

Using Green's function techniques we calculate the spectrum for two optic phonons interacting via anharmonic coupling to two acoustic phonons. The single-phonon density of states, which is related to the first-order Raman spectrum, exhibits a zero (antiresonance) between the individual phonon peaks and yields a line shape in excellent agreement with Scott's recent experimental results for $AlPO_4$.

Quite recent experimental results[1] for the first-order Raman spectrum of $AlPO_4$ have exhibited rather anomalous features in the line shapes associated with optic phonons of the same symmetry. As the temperature is increased the position of the broad peak corresponding to an unstable optic-mode phonon decreases in energy until it is nearly degenerate with another optic phonon which is quite stable. The observed spectrum displays a zero amplitude at an energy between the two optic-phonon energies; however, the position of the zero remains very close to the narrow (stable-phonon) peak. Thus, as the temperature is varied, and the two peaks move close together in energy, the line shape is strongly deformed.[1]

In the present Letter we interpret the above phenomena in terms of the indirect coupling between two optic phonons which is mediated by two acoustic phonons. This interaction can be readily treated by using the Green's function formalism and including explicitly the anharmonic terms in the phonon Hamiltonian.

We begin by considering the Hamiltonian

$$\mathcal{H} = \sum_{\alpha = a,b} \mathcal{H}_{har}^{op(\alpha)} + \mathcal{H}_{har}^{ac} + \mathcal{H}_3, \tag{1}$$

where $\mathcal{H}_{har}^{op(\alpha)}$ refers to the harmonic Hamiltonian for each of the two optic branches labeled by a and b, respectively, i.e.,

$$\mathcal{H}_{har}^{op(\alpha)} = \sum_{\vec{k}} \omega_\alpha^{op}(\vec{k}) [b_{\vec{k}\alpha}^\dagger b_{\vec{k}\alpha} + \tfrac{1}{2}]. \tag{2}$$

In Eq. (2) the phonon creation and destruction operators are denoted by $b_{\vec{k}\alpha}^\dagger$ and $b_{\vec{k}\alpha}$, respectively, and the optic-mode energy is given by $\omega_\alpha^{op}(\vec{k})$. A similar definition holds for $\mathcal{H}_{har}^{ac}$, which represents the harmonic contribution of the acoustic phonons.

The anharmonic term $\mathcal{H}_3$ contains combinations of three phonon operators and is responsible for two distinct physical effects:

(a) This term contributes to the finite lifetime of the optic phonons due to the possible decay of a single optic phonon into two acoustic phonons. The lifetime, and therefore the strength of the

$\mathcal{H}_3$ coupling, can be estimated from the optic-phonon broadening observed experimentally.

(b) The $\mathcal{H}_3$ term provides an indirect coupling between two optic phonons via the anharmonic interaction of each optic phonon with two acoustic phonons. The latter coupling process forms the basis for the present study.

For the third-order term $\mathcal{H}_3$ we consider a model Hamiltonian of the form[2]

$$\mathcal{H}_3 = \sum_{\alpha = a,b} g_\alpha V^{-1/2} \int \Phi^{ac}(x) \Phi^{ac}(x) \Phi_\alpha^{op}(x) d^3x, \tag{3}$$

where the $\Phi(x)$ are the usual phonon-field operators[3] given by

$$\Phi(x) = V^{-1/2} \sum_{\vec{k}} [\omega(\vec{k})/2]^{1/2} \{ b_{\vec{k}} e^{i[\vec{k}\cdot\vec{x} - \omega(\vec{k})t]}$$
$$+ b_{\vec{k}}^\dagger e^{-i[\vec{k}\cdot\vec{x} - \omega(\vec{k})t]} \}; \tag{4}$$

V denotes the crystal volume. Since we are concerned with the first-order Raman spectrum, we need to consider phonons with momentum $\vec{k} \cong 0$. Therefore, for the case under consideration, it is a good approximation to neglect the momentum dependence of the anharmonic coupling coefficient g_α. We have made this assumption in writing the anharmonic term in the form given in Eq. (3).[4]

The fourth-order anharmonic terms in the Hamiltonian will renormalize the single-phonon energies and, on the other hand, contribute to indirect phonon coupling mediated by three other phonons. These, and higher order, processes can be treated by an extension of the theory and will modify the values of the parameters which appear in the final results of the present work.

The strength of the first-order Raman scattering is determined by the phonon correlation function $\langle [A\Phi_a^{op}(x) + B\Phi_b^{op}(x)][A\Phi_a^{op}(x') + B\Phi_b^{op}(x')] \rangle$, where A and B are related to the Raman activity of the respective phonon modes.[5] Since the thermal energies attainable experimentally are negligible compared with the phonon energies under consideration, we employ the Green's function formalism for zero temperature. Effects of finite temperature, such as the softening of the

unstable optic-mode phonon, will henceforth be taken into account by considering the renormalized optic energies $\omega_\alpha{}^{\mathrm{op}}(\vec{k})$ and coupling coefficients g_α as temperature-dependent parameters. In this case the spectral function corresponding to the above correlation function can be expressed in terms of the zero-temperature Green's function:

$$D^{\{A,B\}} = -i\langle T\{(A\Phi_a{}^{\mathrm{op}} + B\Phi_b{}^{\mathrm{op}})$$

$$\times (A\Phi_a{}^{\mathrm{op}} + B\Phi_B{}^{\mathrm{op}})\}\rangle, \qquad (5)$$

where T denotes the time-ordering operator. Then the intensity of the Raman scattering can be related to to the spectral function

$$\rho^{\{A,B\}}(\omega) = -\mathrm{Im}D^{\{A,B\}}(\vec{k}=0,\,\omega). \qquad (6)$$

In terms of the individual phonon Green's functions

$$D_{\alpha\beta}{}^{\mathrm{op}}(x-x') = -i\langle T\{\Phi_\alpha{}^{\mathrm{op}}(x)\Phi_\beta{}^{\mathrm{op}}(x')\}\rangle, \qquad (7)$$

the spectral function takes the form

$$\rho^{\{A,B\}}(\omega) = -\mathrm{Im}[A^2 D_{aa}{}^{\mathrm{op}} + AB(D_{ab}{}^{\mathrm{op}} + D_{ba}{}^{\mathrm{op}})$$

$$+ B^2 D_{bb}{}^{\mathrm{op}}]. \qquad (8)$$

In order to calculate the effects of the anharmonic coupling on the spectral function we consider the infinite set of diagrams shown in Fig. 1. These diagrams demonstrate the indirect optic-phonon coupling mediated by the anharmonic interaction with two acoustic phonons. The bare two-acoustic-phonon Green's function $D_2{}^{(0)\mathrm{ac}}(\vec{K}=\vec{k},\,\omega)$, represented by the solid bubbles in Fig. 1, has been previously calculated.[2] For the
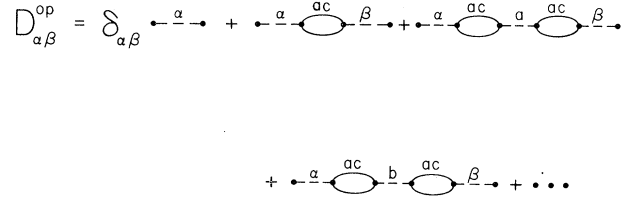

FIG. 1. Diagrammatic representation for the single-optic-phonon propagator $D_{\alpha\beta}{}^{\mathrm{op}}$ including the indirect interaction of optic phonons (dotted lines) via anharmonic coupling to two acoustic phonons. Solid bubbles designate the two-acoustic-phonon Green's function. The interactions are considered in the random phase approximation.

case when the optic-phonon energies fall inside (but not too close to the top of) the two-acoustic-phonon continuum, the two-phonon Green's function can be considered as purely imaginary, and can be expressed as[6]

$$D_2{}^{(0)\mathrm{ac}}(\vec{K}\cong 0,\,\omega) = i\Omega(\omega), \qquad (9)$$

where Ω is a smooth function of energy. The above approximations in the calculation of the acoustic-phonon Green's function neglect structure near the top of the acoustic spectrum which is associated with two-phonon resonances.[2] In situations where the optic-phonon energies are nearly degenerate with such resonances, hybridization of these phonon states can occur and modify the spectrum in an essential fashion.[2]

Turning now to the calculation of the single-optic-phonon propagator we write the one-particle Green's function corresponding to the diagrams shown in Fig. 1:

$$D_{\alpha\beta}{}^{\mathrm{op}}(\vec{k},\,\omega) = \delta_{\alpha\beta}D_\alpha{}^{(0)\mathrm{op}}(\vec{k},\,\omega) + g_\alpha g_\beta \frac{D_\alpha{}^{(0)\mathrm{op}}(\vec{k},\,\omega)D_2{}^{(0)\mathrm{ac}}(\vec{K}=\vec{k},\,\omega)D_\beta{}^{(0)\mathrm{op}}(\vec{k},\,\omega)}{1 - \sum\limits_{\gamma=a,b} g_\gamma{}^2 D_2{}^{(0)\mathrm{ac}}(\vec{K}=\vec{k},\,\omega)D_\gamma{}^{(0)\mathrm{op}}(\vec{k},\,\omega)}. \qquad (10)$$

Following the usual notation,[3] we introduce a propagator for a single phonon,

$$D_\alpha{}^{(0)\mathrm{op}}(\vec{k},\,\omega) = \frac{\omega_\alpha(\vec{k})}{2}\left[\frac{1}{\omega - \omega_\alpha(\vec{k}) + i\delta} - \frac{1}{\omega + \omega_\alpha(\vec{k}) - i\delta}\right]; \qquad (11)$$

it should be noted that $D_\alpha{}^{(0)\mathrm{op}}$ represents an optic phonon with an infinite lifetime.

Broadening of the optic-mode phonons due to the $\mathcal{K}_3$ term is included directly in the Dyson equation (10). As the separation in energy of the two optic phonons is small in comparison with their sum, we consider only the first term on the right-hand side of Eq. (11). Finally, making use of Eqs. (8)-(11), we obtain the optic-phonon spectral function,

$$\rho^{\{A,B\}}(\omega) = \frac{[Ag_a'\Delta_b + Bg_b'\Delta_a]^2}{4\Delta_a{}^2\Delta_b{}^2\Omega(\tilde{\omega})\Omega^{-1}(\omega) + [g_a'^2\Delta_b + g_b'^2\Delta_a]^2\Omega(\omega)\Omega^{-1}(\tilde{\omega})}, \qquad (12)$$

where $\Delta_a = 1 - \omega/\omega_a$, $\Delta_b = 1 - \omega/\omega_b$; $g_\alpha' = g_\alpha[\Omega(\tilde{\omega})]^{1/2}$ is a dimensionless coupling constant and $\tilde{\omega} = \frac{1}{2}(\omega_a + \omega_b)$. It is apparent from Eq. (12) that the spectrum displays an antiresonance feature; i.e., $\rho^{\{A,B\}}(\omega)$
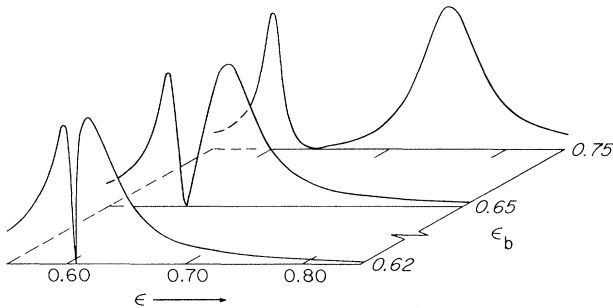
FIG. 2. Single-optic-phonon spectrum plotted as a function of energy ϵ for three positions of the unstable-optic-phonon energy: $\epsilon_b = 0.75$, 0.65, and 0.62. The stable optic peak is centered at $\epsilon_a = 0.60$, and the dimensionless anharmonic coupling coefficients were chosen as $g_a' = 0.13$ and $g_b' = 0.20$ for all three curves. The ratio of the Ramam activities of the two phonons is taken to be $A/B = 0.4$, and the spectrum amplitude is displayed in arbitrary units.

vanishes identically at an energy $\omega = (Ag_a + Bg_b)/(Ag_a\omega_b{}^{-1} + Bg_b\omega_a{}^{-1})$, which lies between the two optic energies ω_a and ω_b. As long as $\omega_a \neq \omega_b$, it is interesting to note that the antiresonance feature exists for arbitrary values of the Raman activity strengths A and B, and the position of the zero is independent of the two-acoustic-phonon propagator.[6] In Fig. 2, the spectral function is plotted as a function of energy for various values of the optic-phonon frequencies. The coupling coefficients g_α', the energies ω_α, and the Raman strength ratio A/B were chosen to produce a spectrum resembling Scott's experimental results for $AlPO_4$.[1] For convenience, dimensionless energy parameters $\epsilon_\alpha = \omega_\alpha/\omega_0$ have been introduced, in terms of an arbitrary scaling energy ω_0. In the figure the curve for $\epsilon_a = 0.60$ and $\epsilon_b = 0.75$ displays two symmetric peaks associated with the optic phonons.[7] Note that the antiresonance feature appears quite near the narrow peak even though the optic phonons are well separated in energy. As the broad peak shifts to $\epsilon_B = 0.65$, corresponding to a temperature increase in the experiment, the antiresonance feature becomes quite prominent and distorts the line shape significantly. Lastly, when the optic-phonon energies are quite close ($\epsilon_a = 0.60$, $\epsilon_b = 0.62$), the broad peak is strongly deformed and a rather sharp antiresonance occurs. These features are in remarkable agreement with the structure in the Raman spectrum observed experimentally.[1]

In conclusion we note that the indirect coupling of unstable optic phonons may be of special interest in the case of ferroelectric materials. In these materials an optic-mode phonon shows a very strong temperature dependence which is connected with the ferroelectric phase transition.[8]

We are indeed grateful to Dr. J. F. Scott for stimulating our interest in this problem and for valuable discussions regarding the importance of the possible coupling between two optic phonons.

Note added in proof. — The antiresonance and associated optical-phonon structure observed in the Raman spectrum of $AlPO_4$ cannot be observed in reflectivity experiments (both peaks correspond to phonons with A_1 symmetry which is not infrared active). In general, however, anharmonic phonon coupling can substantially modify the infrared dispersion as shown by A. S. Barker and J. J. Hopfield, Phys. Rev. 135, A1732 (1964).

[1]J. F. Scott, preceding Letter [Phys. Rev. Letters 24, 1107 (1970)].

[2]J. Ruvalds and A. Zawadowski, Phys. Rev. (to be published).

[3]A. A. Abrikosov, L. P. Gor'kov, and I.-E. Dzyaloshinski, Methods of Quantum Field Theory in Statistical Physics, translated and edited by R. Silverman (Prentice-Hall, Englewood Cliffs, N. J., 1963).

[4]Formally, the general expression for the third-order anharmonic interaction is given as [e.g., see G. Leibfried and W. Ludwig, Solid State Phys. 12, 276 (1961)]

$$\mathfrak{K}_3 = (3!N)^{-1} \sum_{\vec{k}_1\vec{k}_2\vec{k}_3, s_1 s_2 s_3} \Phi_{s_1 s_2 s_3}{}^{\vec{k}_1\vec{k}_2\vec{k}_3} a_{\vec{k}_1 s_1} a_{\vec{k}_2 s_2} a_{\vec{k}_3 s_3},$$

where the $a_{\vec{k}s}$'s are related to the phonon operators by $a_{\vec{k}s} = [2\omega_s(\vec{k})]^{-1/2}(b_{\vec{k}s}{}^\dagger + b_{\vec{k}s})$ with the convention $\hbar = 1$. The coupling coefficient g_α can be related to the crystal force constants implicit in Φ by straightforward substitution of the field operators $\;(x)$ into Eq. (3) to obtain the corresponding expression for $\mathfrak{K}_3$.

[5]For a discussion of the related problem of neutron scattering by phonons see, for example, L. Van Hove, Phys. Rev. 95, 249 (1959).

[6]Using the results of Ref. 2, it can be shown that in the limit of vanishing acoustic-phonon width $\Gamma \to 0$, the two-phonon Green's function becomes

$$D_2^{(0)\mathrm{ac}} = -\tfrac{1}{4} i \pi \omega^2 \rho_{1\frac{1}{2}}\omega,$$

where ρ_1 is the single-acoustic-phonon density of states. For convenience we consider only one acoustic-phonon branch. Inclusion of the real part of $D_2^{(0)\mathrm{ac}}$ (with a finite phonon width Γ) introduces minor modifications in the structure of the optic-phonon line shape, but does not affect the validity of our final result for the position of the antiresonance [Eq. (12)].

[7]For convenience in computation we have taken $\Omega(\omega)$

$= \Omega(\tilde{\omega})$. If the optic-phonon energies are near the top of the two-acoustic-phonon continuum, the energy dependence of $\Omega(\omega)$ cannot be neglected and will induce an asymmetry in the single-optic-phonon spectrum as discussed in Ref. 2.

[8]W. Cochran, Advan. Phys. 9, 387 (1960).

CHEMICAL SHIFTS OF ACCEPTOR BINDING ENERGIES AND g FACTORS IN Si AND Ge

J. C. Phillips

Bell Telephone Laboratories, Murray Hill, New Jersey 07974

Chemical shifts of impurity binding energies and g factors are explored within the framework of a modified effective-mass or wave-packet formalism. Magnitudes of the shifts are determined from band-defect energies, a crystallographic generalization of the quantum-defect method for spherical potentials. Good agreement with experiment is obtained for group-III acceptors in Si and Ge.

The problem of shallow impurity states in semiconductors has attracted much interest and has led to the development[1] of a theory of crystallographic wave packets which is called the effective-mass approximation (EMA). The formalism gives an exhaustive account of all the effects of external perturbations (electric, magnetic, and strain fields) and weak internal hydrogenic potentials which can be explained in terms of symmetry properties alone. Notably absent from the theory so far, however, is any prescription for explaining chemical trends in ground-state properties of impurities. In this Letter a simple Ansatz is introduced which permits exploration of these trends. The method is applied to group-III acceptors X ($X =$ B, Al, Ga, In, Tl) in Si and Ge and is used to discuss chemical trends in ground-state ionization energies $E_I{}^a(X)$ and g factors $g(X)$.

Our model for the impurity potential is the following. Construct a unit cell of volume $\Omega = \frac{1}{4}a^3$ centered on the impurity, where a is the cubic lattice constant. Outside this unit cell the effective-mass Hamiltonian has the form

$$H_{\text{out}} = T - e^2/\epsilon_0 r + \lambda \vec{L} \cdot \vec{S}, \tag{1}$$

where T is the kinetic energy operator, ϵ_0 is the static electronic dielectric constant, and λ is the spin-orbit coupling parameter. A number of studies[2] of microscopic dielectric properties have shown that ϵ_0 is the appropriate screening factor to use for r in this region.

Inside the unit cell the potential is no longer sperically symmetric. It can, however, be expanded in tetrahedral harmonics, as has been done[3] in various molecular one-center studies of $Z\text{H}_4$, $Z =$ C, Si, Ge, or Sn. Write the potential inside the unit cell as

$$V_{\text{ins}}(\vec{r}) = -e^2/\epsilon_0 r + V_1(r) + a(X)xyz + \cdots. \tag{2}$$

The term $V_1(r)$ represents the breakdown of dielectric screening in the central cell, an effect which is almost isotropic[2] and independent of X. The term of tetrahedral symmetry xyz represents the lowest-order contribution of the nearest-neighbor potentials. The presence of the impurity will also produce a local strain field of quadrupole symmetry which we represent by

$$W(r) = \vec{r} \cdot \overleftrightarrow{S} \cdot \vec{r}\, b(r), \tag{3}$$

where S is the strain tensor.

The kinetic energy operator T is not simply $p^2/2m$, but instead operates in the six-dimensional space obtained as the direct product of $\Gamma_{25'}$ (which represents the Bloch states at $\vec{k} = 0$ which are three-fold orbitally degenerate) and the double group $D_{1/2}$. The two terms which make the largest contribution to T are conventionally represented by[1]

$$F = \frac{\hbar^2}{2m} \frac{|\langle \Gamma_{25'} | \vec{p} | \Gamma_{2'} \rangle|^2}{E_0},$$

$$H_1 = \frac{\hbar^2}{2m} \frac{|\langle \Gamma_{25'} | \vec{p} | \Gamma_{15} \rangle|^2}{E_0'},$$

where the appropriate energy denominators have been given in spectroscopic notation.[4]

Because T is already anisotropic, it is convenient to treat the effects associated with (3) and the last term in (2) by making a unitary transformation and absorbing their effects into F and H_1. This cannot be done simply and exactly, but if we are interested primarily in the direction of chemical trends and their approximate magnitude, such an approach offers several advantages. The dominant terms should again be associated with interactions between $\Gamma_{25'}$ and the lowest excited states $\Gamma_{2'}$ and Γ_{15}. We therefore replace the complicated Hamiltonian containing (3) and