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Spectral density of bulk two-phonon polaritons

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Abstract. A linear response function is derived for a system of photons interacting with two-phonon states. This function determines the electric field spectral density of the corresponding mixed states: two-phonon polaritons. Computations of the spectral density for different values of the anharmonicity and the photon–two-phonon coupling constant are carried out.

1. Introduction

The interaction of electromagnetic waves with many-particle excitations in solids has attracted increasing attention in recent years. The linear coupling of polar excitations to electromagnetic waves in infinite media leads to the formation of mixed states known as bulk polaritons. Thus, transverse polar two-phonon states contain a photon admixture and are essentially two-phonon polaritons. Their spectra have been investigated experimentally by small-angle Raman scattering [1–8].

A theory of small-angle Raman scattering from two-phonon states has been developed in [9] in the context of the polariton Fermi resonance theory [10]. The latter describes the interaction of a polariton branch associated with a fundamental vibration with nearby two-phonon states. The photon–two-phonon interaction in that case is mediated by the anharmonic Fermi resonance interaction between the single-phonon and the two-phonon states. When the two-phonon transitions have non-zero dipole moments [11], a direct phonon–two-phonon interaction takes place and leads to the formation of two-phonon polariton states. The direct interaction is of a more general nature than the Fermi resonance one, since it does not involve any degeneracy in the phonon spectrum of the crystal.

Two-phonon polariton spectra are characterized by a strong wavevector dependence (dispersion) in the resonant region and a considerable broadening (damping) in the two-phonon band. The damping of bulk polaritons has been considered in a number of studies [12–15] and the response function approach has proved to be most efficient in the description of their spectra. In the present paper we derive a quantum mechanical expression for the linear response function which determines the spectral density of the electric field of two-phonon polaritons. Computations of the spectral density for different

values of the anharmonicity and the photon–two-phonon coupling constant are carried out.

2. Linear response function for two-phonon polaritons

Linear response functions for bulk polaritons have been derived phenomenologically in [14, 15]. In the case of isotropic media they contain the factor

$$(k^2 - \varepsilon\omega^2/c^2)^{-1} \quad (1)$$

whose imaginary part determines the spectrum of bulk polaritons. One possible way to describe two-phonon polariton spectra is to introduce in (1) an expression for the dielectric function $\varepsilon(\omega)$ appropriate to the two-phonon region. It should be based on model calculations involving Coulomb excitations and neglecting retardation effects. However, as two-phonon polaritons are the true elementary excitations in the considered frequency and wavevector region, a more rigorous approach is to derive a linear response function for the system of photons interacting with two-phonon states.

The relevant Hamiltonian has the following form:

$$H = \sum_k [\hbar\Omega_k b_k^\dagger b_k + \hbar\omega_k a_k^\dagger a_k + AT_k^\dagger T_k - \Gamma_k(T_k^\dagger a_k - a_k^\dagger T_k)] \quad (2)$$

$$T_k = N^{-1/2} \sum_{k_1} b_{k_1} b_{k-k_1} \quad \Gamma_k = \frac{i\hbar}{2} \sqrt{\frac{\omega_k \bar{\Omega}_2 f}{\varepsilon_0}} (\mathbf{e}_k \cdot \mathbf{j}_k)$$

where b_k and a_k are the phonon and photon Bose operators, $\hbar\Omega_k$ and $\hbar\omega_k$ are the corresponding energies, A is the anharmonicity constant and Γ_k is the photon–two-phonon coupling constant. $\hbar\bar{\Omega}_2$ is an average two-phonon energy, $f = \varepsilon_0 - \varepsilon_\infty$ is the dielectric oscillator strength of the two-phonon transitions, and \mathbf{e}_k and \mathbf{j}_k are the polarization unit vectors of the photons and the two-phonon transitions. The photon–single-phonon interaction gives a negligible contribution to two-phonon spectra and, for this reason, terms proportional to ab^\dagger or $a^\dagger b$ are not included in (1).

The electric field operator $E(r)$ in the two-phonon region contains a photon part ($\sim a$) and a polarization part ($\sim T$):

$$E(r) = \sum_k \exp(i\mathbf{k} \cdot \mathbf{r}) [S(k)(a_k - a_{-k}^\dagger) + C(k)(T_k + T_{-k}^\dagger)] \quad (3)$$

$$S(k) = i\sqrt{2\pi\hbar\omega_k/\varepsilon_\infty} \mathbf{e}_k \quad C(k) = -\sqrt{2\pi\hbar\bar{\Omega}_2 f/\varepsilon_0\varepsilon_\infty} \mathbf{j}_k.$$

The electric field spectral density is related to the Fourier components of the retarded Green function D_{ij} defined as

$$D_{ij}(r, r'; t - t') = -i\hbar^{-1} \theta(t - t') \langle [E_i(r, t), E_j(r', t')] \rangle$$

$$\equiv \langle \langle E_i(r, t); E_j(r', t') \rangle \rangle. \quad (4)$$

With the help of (3) its Fourier components are expressed by

$$D_{ij}(k, \omega) = S_i S_j^* \langle \langle a_k; a_k^\dagger \rangle \rangle_\omega + S_i C_j \langle \langle a_k; T_k^\dagger \rangle \rangle_\omega$$

$$+ C_i S_j^* \langle \langle T_k; a_k^\dagger \rangle \rangle_\omega + C_i C_j \langle \langle T_k; T_k^\dagger \rangle \rangle_\omega. \quad (5)$$

As the photon and the two-phonon energies considered here are much higher than

the thermal energy at room temperature, all statistical averages can be replaced by an average over the ground state of the system corresponding to zero temperature. In this case the equations of motion for the Green functions in (5) form a closed linear set whose solution is

$$\langle\langle a_k; a_k^\dagger \rangle\rangle_\omega = (G_\alpha^{-1} - |\Gamma_k|^2 G_T)^{-1} = G_T^{-1} G_\xi \quad (6a)$$

$$\langle\langle a_k; T_k^\dagger \rangle\rangle_\omega = -\langle\langle T_k; a_k^\dagger \rangle\rangle_\omega = \Gamma_k G_\xi \quad (6b)$$

$$\langle\langle T_k; T_k^\dagger \rangle\rangle_\omega = (G_T^{-1} - |\Gamma_k|^2 G_\alpha)^{-1} = G_\alpha^{-1} G_\xi \quad (6c)$$

where

$$G_T = (G_0^{-1} - A)^{-1} \quad G_\alpha = (\hbar\omega - \hbar\omega_k)^{-1} \quad (7)$$

are the two-phonon and the photon Green functions in the absence of photon–two-phonon interaction and

$$G_0(k, \omega) = 2N^{-1}\hbar^{-1} \sum_k (\omega - \Omega_{k_1} - \Omega_{k-k_1})^{-1} \quad (8)$$

is the Green function of two non-interacting phonons.

The spectrum of the mixed photon–two-phonon states (two-phonon polaritons) is determined from the poles of the Green function G_ξ :

$$G_\xi = (G_T^{-1} G_\alpha^{-1} - |\Gamma_k|^2)^{-1}. \quad (9)$$

The energies of the ‘pure’ (with retardation neglected) two-phonon states correspond to the poles of the Green function $G_T(\omega, k)$. Owing to phonon dispersion, the energies of the two-phonon states with a fixed ($k \approx 0$) value of the summary wavevector and different individual wavevectors form a quasi-continuous band (V) of approximately twice the single-phonon band width. In the case of strong anharmonicity (usually $|A/V| > 0.25$ [16, 17]), a narrow peak of two-phonon bound states (a biphonon) splits from the two-phonon band.

It is interesting to note the changes in the photon and the two-phonon Green functions in the case of the photon–two-phonon interaction. Thus the modified photon Green function (6a) has zeros which coincide with the poles of the ‘pure’ two-phonon Green function G_T while the modified two-phonon Green function (6c) has zeros for the frequencies and wavevectors of the ‘pure’ photons. Such changes in the spectrum are typical for the interaction of electromagnetic waves with a continuum of states known as the Fano antiresonance [18].

With the help of (5) and (6) the following expression for the Fourier components of the linear response function is readily obtained:

$$D_{ij}(\omega, k) = G_\xi(\omega, k)[S_i S_j^* G_T^{-1}(\omega, k) + (S_i C_j + C_i S_j)\Gamma_k + C_i C_j G_\alpha^{-1}(\omega, k)] + R(-\omega, -k) \quad (10)$$

where $R(-\omega, -k)$ is the inverse frequency and wavevector part. The two-phonon polariton spectrum is related to the poles of the Green function $G_\xi(\omega, k)$, while the functions G_T^{-1} and G_α^{-1} are regular and monotonic in the considered region. As seen from (9), the poles of G_ξ differ considerably from those of G_T and G_α . The main contribution to the linear response function is associated with the photon part of the electric field ($|S|^2 \gg |C|^2$). It can be shown that this part coincides with the electrodynamic

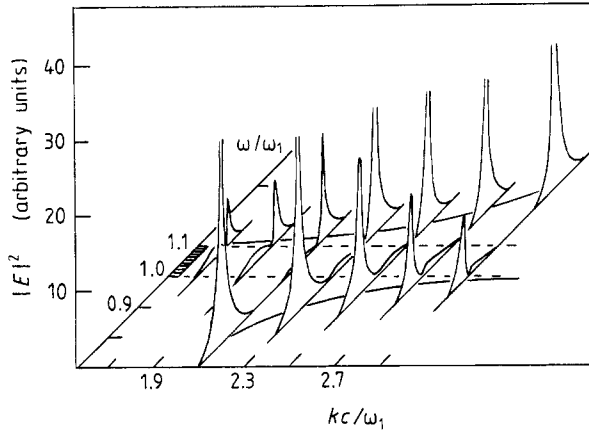


Figure 1. Electric field spectral density of bulk two-phonon polaritons in the region of an intensive two-phonon band of non-interacting phonons.

Green function derived from Maxwell’s equations if the following expression for the dielectric function in the two-phonon region is used:

$$\varepsilon(\omega, k) = \varepsilon_\infty - f\bar{\Omega}_2 G_T(\omega, k). \tag{11}$$

Thus the microscopic approach gives corrections to the two-phonon polariton spectrum associated with the dipole moments of the two-phonon transitions.

3. Electric field spectral density of two-phonon polaritons

The electric field spectral density is related to the imaginary part of the diagonal components of the linear response function by means of

$$\langle |E|^2 \rangle = -\hbar\pi^{-1} \text{Im} \left(\sum D_{ii}(\omega, k) \right). \tag{12}$$

For the computation of the electric field spectral density of two-phonon polaritons, the following integral representation of the Green function of two non-interacting phonons has been employed:

$$G_0 = \int \frac{g_0(\omega') d\omega'}{\hbar(\omega - \omega' + i\eta)} = I(\omega) - i\pi g_0(\omega) \tag{13}$$

where g_0 is the density of states of two non-interacting phonons and $I(\omega)$ is the real part of the integral. A model density of states of elliptical type appropriate to three-dimensional crystals has been used:

$$g_0(\omega) = \begin{cases} \sqrt{(V/2)^2 - \omega^2} & \omega^2 < (V/2)^2 \\ 0 & \omega^2 > (V/2)^2 \end{cases} \tag{14}$$

where V is the two-phonon band width.

The electric field spectral density of two-phonon polaritons has been computed for different values of the oscillator strength and the anharmonicity. The polariton spectrum in the region of an intensive band of two non-interacting phonons is shown in figure 1.

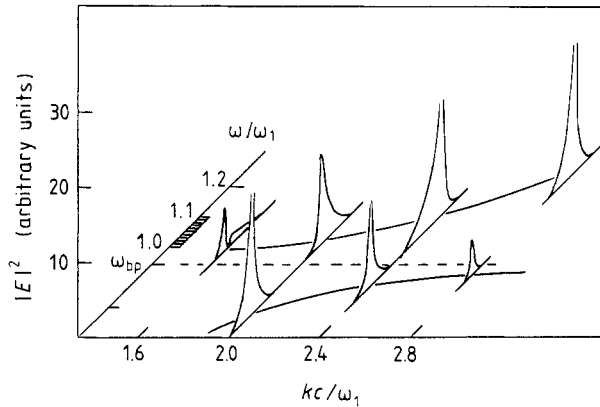


Figure 2. Electric field spectral density of two-phonon polaritons in the case of strong anharmonicity ($A/V = -1$).

For the high-frequency dielectric function the value $\epsilon_{\infty} = 5.75$ has been used corresponding to ZnSe crystals and for the oscillator strength of the two-phonon transition the value $f = 0.15$, which is ten times smaller than that of the 207 cm^{-1} fundamental optical vibration (according to the data cited in [12]). An external damping $\eta = 0.01\bar{\Omega}_2$ has been introduced, leading to finite polariton maxima outside the two-phonon band. The electric field spectral density features bendings of the polariton branches near the band boundaries and a rapid decrease in the intensity with the deviation from the light line corresponding to a decrease in the electromagnetic part of the polariton energy. The intensity inside the two-phonon band is very weak, which is the result of the relatively large dipole moments of the two-phonon transitions.

The presence of anharmonicity may influence strongly the density of two-phonon states and hence the spectrum of two-phonon polaritons. Weak anharmonicity ($|A/V| < 0.25$) leads to a redistribution of the density of two-phonon states inside the band and almost does not change the polariton spectrum outside. Strong anharmonicity ($|A/V| > 0.25$) leading to the formation of a two-phonon bound state (biphonon) outside the band causes considerable changes in the polariton spectrum. A typical two-phonon polariton spectrum in the case of strong anharmonicity ($A/V = -1$) is shown in figure 2 (the other parameters are the same as those used for figure 1). The characteristic polariton features (branch bendings and a gap) appear near the biphonon, while the polariton branch crossing the weak two-phonon band exhibits only an asymmetric broadening.

The small-angle Raman scattering spectrum in the region of a two-phonon band of moderate intensity ($2\nu_4$ in NH_4Cl) measured in [5] is shown in figure 3(b). The quasi-biphonon at the lower end of the band does not have the necessary symmetry F_2 and does not contribute to the Raman spectrum. The corresponding spectral density (figure 3(a)) computed for an oscillator strength $f = 0.03$ reproduces the main features of the observed spectrum, namely the penetration of the polariton branches into the band, the antiresonance (minimum) in the middle of the band and the doublet structure near the upper boundary for $k = 34000 \text{ cm}^{-1}$.

When the polariton spectrum inside the band has a considerable intensity (in the case of small dipole moments of the two-phonon transitions), it will be influenced by the

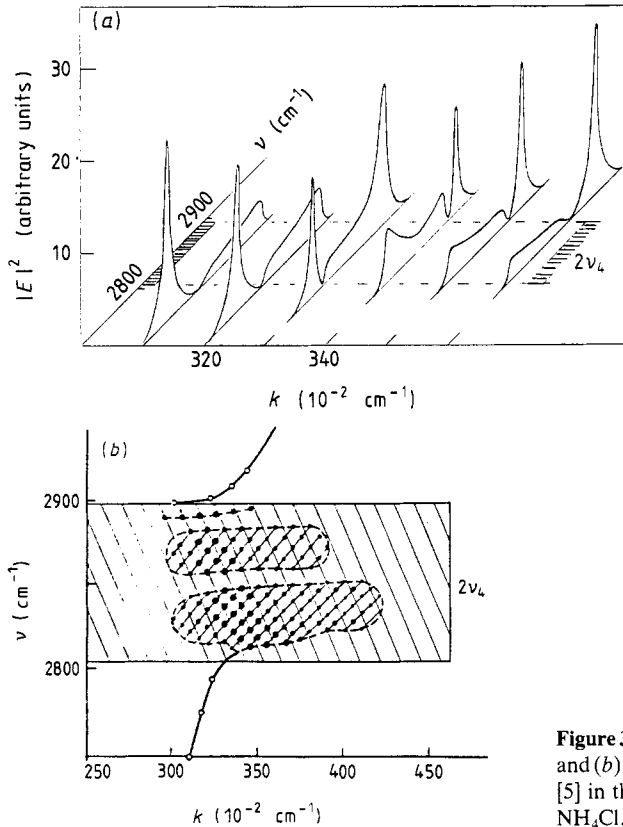


Figure 3. (a) Computed polariton spectral density and (b) small-angle Raman spectrum measured in [5] in the region of the two-phonon band $2\nu_4$ in NH_4Cl .

band structure (critical points and quasi-biphonons). In some cases this may lead to a non-monotonic behaviour of the polariton branch inside the band [11].

4. Conclusion

The analysis of the electric field spectral density shows that the two-phonon polariton spectrum depends on the density of two-phonon states and the dipole moments of the two-phonon transitions. Away from two-phonon resonances, the polariton spectrum coincides with that of the 'pure' photons in the medium. The polariton spectrum near the biphonon is similar to that associated with fundamental vibrations, while owing to the smaller dipole moments of the two-phonon transitions the gap in the polariton spectrum above the biphonon is smaller. The polariton spectrum in the region of intensive two-phonon bands is characterized by strong deviations from the light line (branch bending) outside the band and considerable damping inside. The polariton maxima in the region of weak two-phonon bands follow the light line and are accompanied only by an asymmetric broadening. Our results are in good agreement with the theoretical results in [9] and the experimental results in [5].

References

- [1] Winter F H and Claus R 1972 *Opt. Commun.* **6** 22
- [2] Mavrin B N and Sterin H E 1972a *Fiz. Tverd. Tela* **14** 2801; 1972b *Zh. Exp. Teor. Fiz. Pis. Red.* **16** 265
- [3] Gorelik V S, Mitin G G and Sushchinsky M M 1974 *Fiz. Tverd. Tela* **16** 2956; 1975a *Zh. Exp. Teor. Fiz.* **69** 823; 1975b *Fiz. Tverd. Tela* **17** 2482
- [4] Mitin G G, Gorelik V S, Kulevsky L A, Polivanov U N and Sushchinsky M M 1975 *Zh. Exp. Teor. Fiz.* **68** 1757
- [5] Gorelik V S, Maximov O P, Mitin G G and Sushchinsky M M 1977 *Solid State Commun.* **21** 615
- [6] Akcipetrov O A, Georgiev G M, Mitusheva I V, Michailovski A G and Penin A N 1975 *Fiz. Tverd. Tela* **17** 2027; 1978 *Fiz. Tverd. Tela* **20** 402
- [7] Denisov V N, Mavrin B N, Podobedov V B and Sterin K E 1981 *Solid State Commun.* **40** 693; 1982 *Zh. Exp. Teor. Fiz.* **82** 406
- [8] Fukushi K, Nippus M and Claus R 1978 *Phys. Status Solidi b* **86** 257
- [9] Agranovich V M, Ivanova E P and Lalov I J 1979 *Fiz. Tverd. Tela* **21** 1629
- [10] Agranovich V M and Lalov I J 1971a *Fiz. Tverd. Tela* **13** 1032; 1971b *Zh. Exp. Teor. Fiz.* **61** 656; 1976 *Solid State Commun.* **19** 503
- [11] Lalov I J and Stoychev K T 1979 *Bulg. J. Phys.* **6** 304
- [12] Benson H J and Mills D L 1970 *Phys. Rev. B* **1** 4835
- [13] Loudon R 1972 *J. Phys. A: Math. Gen.* **3** 233
- [14] Barker A S Jr and Loudon R 1974 *Rev. Mod. Phys.* **44** 18
- [15] Loudon R 1977 *Spectroscopia Nonlineare* ed N Bloembergen (Amsterdam: North-Holland)
- [16] Klafter J and Jortner J 1982 *J. Chem. Phys.* **77** 2816
- [17] Belousov M V 1982 *Excitations* ed E I Rashba and M D Sturge (Amsterdam: North-Holland)
- [18] Fano U 1961 *Phys. Rev.* **124** 1866