area of a boundary plane and each line $l_{\alpha\beta}$ passing from nucleus $\alpha$ on, say, the left-hand side of the boundary to $\beta$ on the right-hand side through that area. The sum of the forces $\langle F_{\alpha\beta}\rangle$, one for each line $l_{\alpha\beta}$, gives the value $(Q - Q')/L^3$. The value WMS find for $Q'/L$, viz., $0.03e^2/a^4$, is quite reasonable for this quantity.

In a paper published after the submission of these comments, Wannier and Meissner[4] have argued that the surface contribution for a finite crystal is unlikely to be important. In fact, of course, provided the crystal is large enough so that its density is no longer size dependent, $(Q - Q')/L^3$ must be the same for the finite crystal and for PBC.

In conclusion, we find that the result of WMS is invalid because they used the sum $Q'$ instead of $Q$.

I have benefited from discussions with C. M. Varma and C. Herring's criticism of the manuscript.

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# Comments on Two-Phonon Resonances in Quantum Crystals*

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Recent numerical computations of the phonon spectrum of quantum crystals have demonstrated the existence of an anomalous extra phonon branch which lies above the usual acoustic modes. The purpose of the present note is to explain the physical origin of the anomalous branch in terms of two-phonon resonances, and to discuss briefly the possibility of observing these resonances in quantum crystals by neutron-scattering and Raman-scattering experiments.

It has recently been proposed that the anharmonic interactions between phonons in crystals can give rise to a two-phonon bound state whose energy lies above the two-phonon continuum. Bound phonon pairs exhibit sharp structure in the second-order phonon spectrum as observed in the Raman data on diamond,[1,2] and, in addition, may substantially modify the single-phonon spectrum as observed in the first-order Raman scattering from quartz.[3,4]

Bound states of two phonons are split off above the two-phonon continuum by the repulsive fourth-order anharmonic term in the phonon Hamiltonian providing that the anharmonicity is larger than a critical strength.[5,6] The critical value of the anharmonic strength is related to the nature of the single-phonon dispersion and involves parameters such as the curvature of the phonon spectrum near the top of the single-phonon continuum, and the "bandwidth" of the phonon branch.[5,6] If the anharmonic coupling is weaker than the critical strength, it is still possible to create two-phonon resonances[6] which give rise to considerable modifications in the spectrum within the two-phonon continuum.

The above considerations suggest that the highly anharmonic quantum crystals provide ideal systems for the formation of bound phonon pairs. However, another consequence of large anharmonicity is substantial broadening of the phonon modes which would, in general, obscure the bound-state structure. Nevertheless, if the energy widths of the two-phonon resonances are comparable to the single-phonon widths, it may be possible to observe these resonances experimentally.

Numerical calculations[7,8] of the phonon spectrum of some quantum crystals using the self-consistent harmonic approximation[9] have recently been published. In particular, the calculations for solid neon[7] and solid $^3$He in the bcc phase[8] find a peculiar extra branch in the phonon spectrum which lies above the usual acoustic-phonon modes. Since these crystals are Bravais, the extra branch cannot be attributed to an optical phonon. In the case of $^3$He, as shown in Fig. 1 of Ref. 8, the extra branch is situated at roughly twice the maximal single-acoustic-phonon energies. Furthermore, the anomalous peak has a width comparable to the single-phonon widths, and displays a peculiar momentum dependence.

Leath and Watson[10] have suggested that the anomalous peak may be due to the mixing of one- and two-phonon states via the third-order anharmonic coupling. Using a one-dimensional linear chain model with nearest-neighbor forces, they were able to demonstrate in analytic form the dramatic changes in the single-phonon spectrum associated with the singularity in the joint two-phonon density of states which is a characteristic of their one-dimensional model. It is important to stress that the Leath-Watson theory neglects fourth-order anharmonic terms.

Unfortunately, however, since the unperturbed joint density of states for two acoustic phonons is relatively smooth in the case of three-dimensional solids, the phonon anomaly in quantum crystals cannot be explained simply in terms of structure in the *unrenormalized* two-phonon density of states.

The aim of the present note is to point out that the formation of two-phonon resonances, and subsequent hybridization of the resonance with single phonons, provides an alternate explanation for the physical origin of the anomalous phonon branch in quantum crystals.

As the theory of two-phonon bound states and resonances has been presented elsewhere,[5,6] we shall only outline the theoretical development with emphasis on the physical approximations involved. A very simple model for the form of the anharmonic interaction is to assume that the third- and fourth-order anharmonic terms are described by coupling parameters $g_3$ and $g_4$, respectively, which are independent of momentum. In other words, the model assumes a point interaction between phonons in real space. The model is successful in explaining several features of the Raman spectrum from solids.[6] As a further approximation we assume that near the Brillouin-zone edge (corresponding to the energy region near the top of the acoustic modes) the phonon dispersion is parabolic in nature. With these simplifying assumptions, it is a straightforward matter to calculate analytically both the second- and first-order phonon spectrum including resonances. As discussed in Ref. 6, the calculation proceeds in two parts. First it is instructive to calculate the two-phonon spectrum by solving the Bethe-Salpeter equation for the two-phonon Green's function $D_2$ as shown diagrammatically in Fig. 1(a). The solution involves summing a simple geometric series and is given by

$$D_2(\vec{K},\omega)=4\lambda f/(1-g_4'f)\ , \tag{1}$$

where the constant $\lambda=\alpha\omega_0^2\Delta^{1/2}$ includes a cutoff energy parameter $\Delta$, the maximum acoustic-phonon energy $\omega_0$, and a constant $\alpha$ which describes the unrenormalized single-phonon density of states $\rho_1^{(0)}(\omega)\simeq\alpha(\omega_0-\omega)^{1/2}$. The fourth-order anharmonic coupling is described by the dimensionless parameter $g_4'=\lambda g_4$, and

$$f=\frac{1}{\Delta}\int_0^\Delta\frac{d\omega'(\omega')^{1/2}}{\omega-2(\omega_0-\omega')+i\Gamma}\ . \tag{2}$$

The $f$ function in Eq. (2) contains a single-phonon width $\Gamma$ which is considered to be a phenomenological parameter. It is apparent from Eq. (1) how the formation of a resonance can strongly modify the two-phonon density of states which is proportional to the imaginary part of $D_2$. Namely, a sharp peak corresponding to a resonance will appear at an energy such that $1-g_4'\,\mathrm{Re}f=0$. For details of the second-order spectrum we refer the reader to Ref. 6.[11]

Turning now to the single-phonon spectrum, we shall relate the resonance structure to the anomalous branch in quantum crystals. In this case the third-order anharmonic terms cause a hybridization of the resonance with single phonons as illustrated diagrammatically in Fig. 1(b). The main point is that in the absence of two-phonon resonances (i.e., $g_4'=0$) the solution of the Dyson equation in Fig. 1(b) exhibits only a single peak corresponding to the broadened single acoustic phonon. If on the other hand, one includes the fourth-order coupling ($g_4'\neq0$), a secondary (resonance) peak will appear in the *first-order spectrum*. To illustrate the hybridization effects we write the results of Ref. 6 for the single-phonon density of states:

$$\rho_1(\vec{K},\omega)=-\frac{1}{\pi}\,\mathrm{Im}\frac{1}{\omega-\Omega(\vec{K})[1+(g_3')^2f(1-g_4'f)^{-1}]}\ , \tag{3}$$

where $g_3'=(2\lambda)^{1/2}g_3$ is a dimensionless coupling constant and $\Omega(\vec{K})$ denotes the energy of the single acoustic phonon which is hybridized with the resonance. The $\rho_1(\vec{K},\omega)$ spectrum for various values of the coupling is plotted in Fig. 2, and shows vividly the appearance of an extra peak progressively stronger with increased fourth-order ($g_4'$) anharmonic coupling. Thus the formation of a two-phonon resonance exhibits structure in the first-order phonon spectrum in a manner quite consistent with the anomalous branch in quantum crystals.

Since the resonance structure appears in the *first-order* phonon spectrum, there is a strong possibility of observing the anomalous peaks experimentally. A similar case of phonon hybridization has already

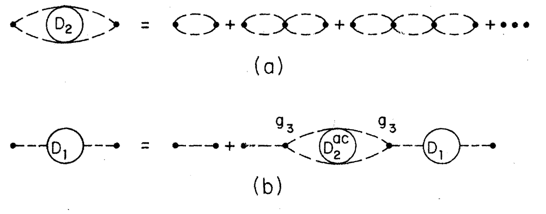

FIG. 1. (a) Bethe-Salpeter equation for the two-phonon propagator $D_2$; (b) diagrammatic representation of the Dyson equation for the single-phonon Green's function $D_1$, showing the hybridization of the single phonon with the two-phonon resonance.

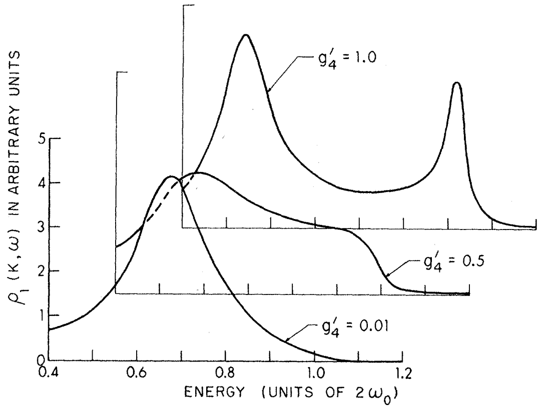

FIG. 2. Single-acoustic-phonon spectrum plotted as a function of energy for various values of the fourth-order anharmonic $g_4'$ coupling. Although the single-phonon width was taken to be rather large ($\Gamma = 0.1\omega_0$), the secondary peak near $2\omega_0$ becomes comparable in intensity to the single-phonon peak as the anharmonic interaction pushed the two-phonon resonance higher than twice the single-phonon energy. Hybridization of the single phonon with the resonance is determined by the third-order coupling which was taken as constant ($g_3' = 0.4$) for all three curves.

been observed in quartz[3,4] by means of Raman scattering. Thus the hcp phase of solid helium, which exhibits a Raman-active optical mode,[12] could display a similar hybridization of the two-acoustic-phonon resonance with the optic mode. However, in the case of quantum crystals with no optic-phonon modes, the light would scatter from the two-phonon resonance by means of a second-order process.

Although the resonance can be expected to be fairly broad (of the order of twice the single-phonon width), the light-scattering experiments may be able to discern the form of the line shape as well as polarization properties. Werthamer's calculation[12] of the light-scattering cross section from solid helium suggests that both one- and two-phonon scattering processes should be observable by Raman scattering. The latter estimates are supported by the recent successful observation of two-roton processes in superfluid helium by Raman-scattering experiments.[13]

Neutron studies of quantum crystals, in particular neon,[14] have provided very accurate determination of the single-phonon spectrum. The latter studies have shown that anharmonic effects are even more pronounced than previous theoretical estimates. Because the two-phonon resonance appears in the first-order spectrum at various momentum values, neutron-scattering experiments would provide an ideal probe of the structure and momentum dependence of the resonance.

Finally, it is worth mentioning that measurements of the phonon spectrum for various pressures would determine how the position and width of the anomalous peak varies with anharmonicity and thereby provide very useful information about phonon interactions in quantum solids.

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