Comment on "Calculation of Phonon-Phonon Interactions and the Absence of Two-Phonon Bound States in Diamond"

The recent Letter of Vanderbilt, Louie, and Cohen[1] (VLC) elegantly confirms that the sharp feature at $\Omega_D = 2667$ cm^{-1} in the two-phonon Raman spectrum of diamond[2] *is not* a two-phonon bound state.[3] However, the work of VLC also reestablishes the anomalous nature of that feature since they correctly note that its position relative to the zone-center phonon at[2] $\omega_D(\Gamma) = 1332.5$ cm^{-1} has not yet been accounted for, i.e., $\Omega_D - 2\omega_D = 2$ cm$^{-1} \neq 0$. Thus, notwithstanding the work of Tubino and Briman (TB),[4] Go, Bilz, and Cardona,[5] Uchinokura, Sekine, and Matsumura,[6] and VLC, there is still no satisfactory explanation of the 2667-cm^{-1} anomaly. Accordingly, I think it would be useful (a) to specify here the key experimental facts which must be collectively accounted for in any future theory which proports to explain what the 2667 cm^{-1} feature *is*, and (b) to point out that a similar and perhaps equally anomalous feature occurs in the Raman spectrum of graphite.[7]

First, note that the anomalous energy of the 2667 cm^{-1} feature which was originally considered suspect has been confirmed in additional independent experiments.[8] Second, a key aspect of the anomaly is that its intensity is proportional to the scattering volume, V, not to V^2.[2] Thus, the interaction giving rise to the 2667-cm^{-1} peak must be described by a "single bubble" Feynman diagram and is not compatible with a "two bubble" event such as would apply to a repeated one-phonon process.[9]

The third point of interest is the polarization character of the 2667-cm^1 feature which exhibits a Raman tensor with the $\Gamma^{(1+)}$ symmetry of the O_h^7 space group. If the 2667-cm^{-1} band is a two-phonon state, its Raman tensor will transform according to a linear combination of the irreducible representations $\Gamma^{(1+)}$, $\Gamma^{(12+)}$, and $\Gamma^{(25+)}$. This linear combination *must* contain $\Gamma^{(1+)}$ if the anomalous feature is an overtone state and *may* contain $\Gamma^{(1+)}$ if it is a combination band. Combinations which exclude $\Gamma^{(1+)}$ can be ruled out on experimental grounds. In any case, an explanation of the dominance of the $\Gamma^{(1+)}$ component must be intrinsic to a successful theoretical analysis of the 2667-cm^{-1} mode. To date, only Go, Bilz, and Cardona[5] have accounted theoretically for the $\Gamma^{(1+)}$ polarization of the 2667-cm^{-1} band, but they too have not explained its anomalous position.

Finally, the calculations of TB[4] and VLC[1] show that the one-phonon dispersion curves of diamond have a maximum along the Δ (100) direction rather than at the zone-center Γ point. It is interesting to note that hexagonal graphite, another crystalline form of carbon, also exhibits one-phonon dispersion curves which are not maximal at the zone center.[10] Like diamond, graphite shows a very sharp, high-energy, two-phonon Raman band at $\Omega_G = 3248$ cm^{-1}, but this band is much more dramatically shifted up relative to the zone-center phonon at $\omega_G = 1581 \pm 1$ cm^{-1}, i.e., $\Omega_G - 2\omega_G(\Gamma) = 86$ cm^{-1}.[7] Though the 3248-cm^{-1} feature of the Raman spectrum of graphite has not attracted the theoretical attention which has been lavished upon the 2667-cm^{-1} feature of diamond, it is equally intriguing. Once the upper branches of the one-phonon dispersion curves of graphite are measured experimentally, we may find that the 3248-cm^{-1} band is as anomalous and worthy of explanation as is the 2667-cm^{-1} band of diamond.

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