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

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We demonstrate that anharmonic phonon-phonon coupling constants can be extracted from frozen-phonon total-energy calculations. The method is applied to the optical modes of diamond. The zone-center coupling constants are completely determined through fourth order, and are used to compute an effective four-phonon vertex including virtual optical-phonon exchange. The interaction is found to have the *wrong sign* to allow formation of a two-phonon bound state.

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Recently, several researchers have demonstrated the feasibility of calculating phonon frequencies from first principles by evaluating the total energy for a series of frozen-phonon geometries.[1-3] However, it is not as widely appreciated that the same approach can be used to determine higher-order anharmonic terms in the phonon Hamiltonian.[1,4] In this Letter we report the first systematic calculation of this kind, a determination of the third- and fourth-order anharmonic coupling constants for optical phonons in diamond. The calculation is done with a self-consistent localized-orbital approach to local-density-functional theory.[5]

To date, no reliable experimental or theoretical information has been available on these optical anharmonic terms. Measurements of anharmonic elastic moduli, thermal expansion and thermal conductivity, phonon linewidths, and pressure or stress dependencies of phonon frequencies (Grüneisen parameters) can only give information about purely acoustical or mixed acoustical-optical interactions. Theoretically, empirical Born- or Keating-type force-constant models are inadequate, since there is no reason to expect their range of validity to extend beyond the harmonic approximation. Yet, these optical anharmonic terms are of great interest. Some fifteen years ago, Cohen and Ruvalds[6] pointed out that a sufficiently strong positive fourth-order coupling could give rise to a two-phonon bound state, which in turn could provide an explanation for an anomalous peak in the two-phonon Raman spectrum of diamond.[7] Alternative explanations have been proposed,[8] and the bound-phonon model has remained controversial. The calculations presented here demonstrate that the phonon coupling is actually *negative*, in which case the two-phonon bound state cannot form in diamond.

For an optical zone-center frozen phonon, the atomic displacements are

$$\vec{\xi}(1)=\vec{u};\quad \vec{\xi}(2)=-\vec{u} \tag{1}$$

for atoms 1 and 2, respectively. Defining the derivatives of the energy per cell E/N as

$$E_x = N^{-1}\,dE/du_x,$$

etc., we can expand the energy in a Taylor series as

$$\frac{E}{N}=\frac{E_0}{N}+\frac{1}{2!}\sum_{\lambda\lambda'}E_{\lambda\lambda'}u_\lambda u_{\lambda'}+\frac{1}{3!}\sum_{\lambda\lambda'\lambda''}E_{\lambda\lambda'\lambda''}u_\lambda u_{\lambda'}u_{\lambda''}+\cdots, \tag{2}$$

where λ labels the polarizations x,y,z. The only distinct nonzero elastic constants up to fourth order allowed by the diamond crystal symmetry are

$$\kappa=(1/2!)E_{xx},\quad \gamma=(1/3!)E_{xyz},$$
$$\alpha=(1/4!)E_{xxxx},\quad \beta=(1/4!)E_{xxyy}. \tag{3}$$

Figure 1 illustrates the extraction of these constants. In Fig. 1(a), we plot $\Delta E(\vec{u})=[E(\vec{u})-E_0]/N$ vs u for displacements along the $\hat{u}\parallel(100)$ direction. To obtain the Taylor coefficients, we expand the region near $u=0$ in Fig. 1(b), plotting $\Delta E/u^2$ vs u^2. Then the intercept at $u^2=0$ gives the harmonic term κ, and the asymptotic slope gives α. We also show in Fig. 1(b) simi-

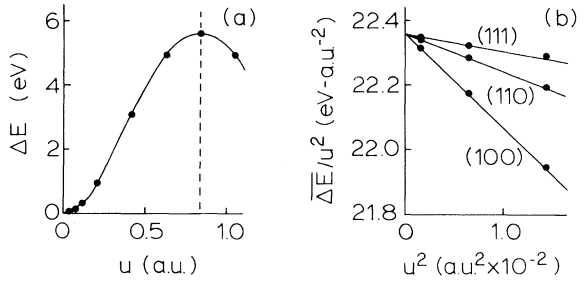

FIG. 1. (a) Energy change per cell vs displacement in the (100) direction for a zone-center optical phonon. Dots represent the calculated points; the energy curve is symmetric about the dashed line. (b) Same data, now for several directions, plotted on rescaled axes (see text), showing asymptotes at the origin.

lar plots for $\hat{u}$ in the (110) and (111) directions; in the latter case, there is no even symmetry, and so we replace ΔE by $\overline{\Delta E} = [\Delta E(\vec{u}) + \Delta E(-\vec{u})]/2$. It can be shown that the asymptotic slopes are $(\alpha + 3\beta)/2$ and $(\alpha + 6\beta)/3$ for the (110) and (111) directions, respectively. The fact that the intercepts coincide in Fig. 1(b) is reassuring, and the fact that the curves are nearly linear indicates that sixth- and higher-order terms are not yet important. Finally, γ can be extracted from the odd component of ΔE in the (111) direction. We find

$$\kappa = 22.36 \text{ eV a.u.}^{-2}, \quad \gamma = 24.49 \text{ eV a.u.}^{-3},$$
$$\alpha = -28.98 \text{ eV a.u.}^{-4}, \quad \beta = 2.08 \text{ eV a.u.}^{-4}. \tag{4}$$

This completes the determination of the optical zone-center elastic coupling constants up to fourth order. The value of κ implies a zone-center phonon frequency of 1344 cm^{-1}, in excellent agreement with the experimental value of 1332 cm^{-1}. This agreement gives us confidence in the accuracy of the calculated third- and fourth-order constants, for which no experimental comparison is available. The result that α is strongly negative can be understood by examining Fig. 1(a). A displacement of $u = a/2$ maps the crystal back into itself, and the energy curve is required to be symmetric about $u = a/4 = 0.84$ a.u. The calculated curve has, plausibly, a cosinelike form; we would then expect alternating signs ($E_{xx} > 0$, $E_{xxxx} < 0$, etc.) for the derivatives. This is precisely what we find. Several empirical force-field models which attempt to go beyond the harmonic approximation have been proposed[9,10]; however, models of this type contain a bond-stretching term and generally give the wrong sign for α, because they cannot reproduce the periodic nature of $\Delta E(u)$ without introducing unphysical cusps where the bonds are redefined at $u = a/4$. The *ab initio* optical-phonon parameters of Eq. (4) should be useful in constraining future attempts at such models.

Let us now make the connection to the phonon-phonon interaction amplitudes. The phonon Hamiltonian may be written[11]

$$H = E_0 + H_2 + H_3 + H_4 + \ldots,$$

where

$$H_2 = T + \frac{1}{2!}\sum_{\substack{\vec{k}\vec{k}' \\ \lambda\lambda'}} \Phi_{\lambda\lambda'}^{\vec{k}\vec{k}'} a_{\vec{k}\lambda} a_{\vec{k}'\lambda'} = \sum_{\vec{k}\lambda} \hbar\omega(\vec{k},\lambda)\left(b_{\vec{k}\lambda}^{\dagger} b_{\vec{k}\lambda} + \tfrac{1}{2}\right),$$

$$H_3 = \frac{1}{3!}\frac{1}{(2N)^{1/2}}\sum_{\substack{\vec{k}\vec{k}'\vec{k}'' \\ \lambda\lambda'\lambda''}} \Phi_{\lambda\lambda'\lambda''}^{\vec{k}\vec{k}'\vec{k}''} a_{\vec{k}\lambda} a_{\vec{k}'\lambda'} a_{\vec{k}''\lambda''}, \tag{5}$$

$$H_4 = \frac{1}{4!}\frac{1}{2N}\sum_{\substack{\vec{k}\vec{k}'\vec{k}''\vec{k}''' \\ \lambda\lambda'\lambda''\lambda'''}} \Phi_{\lambda\lambda'\lambda''\lambda'''}^{\vec{k}\vec{k}'\vec{k}''\vec{k}'''} a_{\vec{k}\lambda} a_{\vec{k}'\lambda'} a_{\vec{k}''\lambda''} a_{\vec{k}'''\lambda'''}.$$

The normal-mode coordinates have been quantized as

$$a_{\vec{k}\lambda} = \left(\frac{\hbar}{2M\omega(\vec{k},\lambda)}\right)^{1/2}\left(b_{\vec{k}\lambda} + b_{-\vec{k},\lambda}^{\dagger}\right) \tag{6}$$

and we have made use of

$$\Phi_{\lambda\lambda'}^{\vec{k}\vec{k}'} = \delta_{\lambda\lambda'}\delta_{\vec{k},-\vec{k}'} M\omega^2(\vec{k},\lambda).$$

The Φ are the bare anharmonic coupling constants which determine the multiphonon scattering amplitudes, e.g.,

$$\langle \vec{k}_3\lambda_3, \vec{k}_4\lambda_4 | H_4 | \vec{k}_1\lambda_1, \vec{k}_2\lambda_2 \rangle = \frac{\hbar^2}{8NM^2}[\omega_1\omega_2\omega_3\omega_4]^{-1/2}\Phi_{\lambda_1,\lambda_2,\lambda_3,\lambda_4}^{-\vec{k}_1,-\vec{k}_2,\vec{k}_3,\vec{k}_4}. \tag{7}$$

The frozen phonon of Eq. (1) is given by

$$a_{\vec{k}\lambda}=\begin{cases}(2Nu_\lambda)^{1/2}, & \vec{k}=0;\\ 0, & \text{otherwise.}\end{cases} \tag{8}$$

Substituting in Eq. (5) and comparing with Eq. (2), we find

$$\Phi^{00}_{xx}=M\omega^2=\kappa, \quad \Phi^{000}_{xyz}(3!/2)\gamma, \quad \Phi^{0000}_{xxxx}=(4!/2)\alpha, \quad \Phi^{0000}_{xxyy}=(4!/2)\beta. \tag{9}$$

To see how these multiphonon scattering amplitudes bear on the question of the phonon bound state, we follow Ref. 6 in considering the variational two-phonon wave function

$$|\Psi_2\rangle=\sum_{\vec{k}\lambda}\phi(\vec{k},\lambda)|\vec{k}\lambda,-\vec{k}\lambda\rangle, \tag{10}$$

where $\phi(\vec{k},\lambda)$ is the bound-state envelope.[12] The dispersion relation $\omega(\vec{k},\lambda)$ is assumed to have an absolute maximum ω_0 at Γ, so that

$$\Delta E_2=\langle\Psi_2|H_2|\Psi_2\rangle-2\hbar\omega_0<0.$$

However, the fourth-order anharmonic coupling gives rise to an energy shift

$$\Delta E_4=\langle\Psi_2|H_4|\Psi_2\rangle=\frac{\hbar^2}{8NM^2\omega_0^2}\sum_{\substack{\vec{k}\vec{k}'\\ \lambda\lambda'}}\phi^*(\vec{k}',\lambda')\phi(\vec{k},\lambda)\Phi^{\vec{k},-\vec{k},\vec{k}',-\vec{k}'}_{\lambda,\lambda,\lambda',\lambda'}. \tag{11}$$

The envelope function ϕ must be strongly localized near Γ, because the two-phonon state is at most weakly bound (weakly localized in real space). Since the coupling Φ is an analytic, i.e., smooth, function of the $\vec{k}$ indices,[13] it is a good approximation to replace the coupling in Eq. (11) by $\Phi^{0000}_{\lambda\lambda\lambda'\lambda'}$. Then it is easy to see that if α and β were strongly positive, ΔE could shift the expectation value $\langle\Psi_2|H_2+H_4|\Psi_2\rangle$ above the top of the two-phonon continuum. The variational estimate is a lower bound, and so the state would necessarily exist, and would provide a natural explanation for the anomalous two-phonon Raman peak observed ~ 2 cm^{-1} above $2\omega_0$. In reality, however, the strongly negative value of α in Eq. (4) is likely to dominate Eq. (11), making the bound state very unlikely.

So far we have omitted the influence of the third-order coupling which enters in perturbation theory and gives rise to a renormalization to the fourth-order term,

$$\langle\vec{k}_3\lambda_3,\vec{k}_4\lambda_4|H_4'|\vec{k}_1\lambda_1,\vec{k}_2\lambda_2\rangle=\sum_{\Psi_j}\langle\vec{k}_3\lambda_3,\vec{k}_4\lambda_4|H_3|\Psi_j\rangle\frac{1}{E_{12}-E_j}\langle\Psi_j|H_3|\vec{k}_1\lambda_1,\vec{k}_2\lambda_2\rangle. \tag{12}$$

One-, three-, and five-phonon intermediate states must be considered,[14] as shown in Fig. 2. As long as the external lines have small $\vec{k}$, the virtual phonons must also, because of $\vec{k}$ conservation at the vertices. Thus it is consistent with the earlier discussion to make the approximations

$$\Phi^{\vec{k}\vec{k}'\vec{k}''}_{\lambda\lambda'\lambda''}\approx\Phi^{000}_{\lambda\lambda'\lambda''}, \quad E_{12}-E_j\approx\hbar\omega(2-n_j), \tag{13}$$

where n_j is the number of phonons in Ψ_j. Diagrams 2(c)–2(f) contribute to scatterings of the type $xy\rightarrow xy$, etc., with the result

$$\langle\vec{k}_3x,\vec{k}_4y|H_4'|\vec{k}_1x,\vec{k}_2y\rangle=-\frac{\hbar^2}{12NM^3\omega_0^4}(\Phi^{000}_{xyz})^2. \tag{14a}$$

Similarly diagrams 2(a)–2(d) contribute for scatterings $xx\rightarrow yy$, etc., so that

$$\langle\vec{k}_3y,\vec{k}_4y|H_4'|\vec{k}_1x,\vec{k}_2x\rangle=-\frac{\hbar^2}{4NM^3\omega_0^4}(\Phi^{000}_{xyz})^2. \tag{14b}$$

Comparison with Eq. (7) and use of (9) yield the renormalized fourth-order constants

$$\begin{aligned}&\alpha'=\alpha=-28.98\text{ eV a.u.}^{-4}, \quad \beta'=\beta-\gamma^2/2\kappa=-11.33\text{ eV a.u.}^{-4},\\ &\beta''=\beta-3\gamma^2/2\kappa=-38.16\text{ eV a.u.}^{-4},\end{aligned} \tag{15}$$

where β' and β'' describe $xy\rightarrow xy$ and $xx\rightarrow yy$ processes, respectively. It is now clear that *all* of the renormalized fourth-order interactions are strongly negative; this result appears to rule out the existence of the two-phonon bound state in diamond.

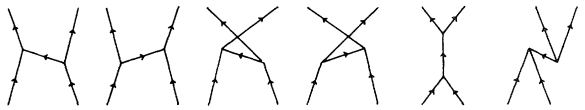

FIG. 2. Feynman diagrams in which exchange of a virtual optical phonon contributes to the renormalized four-phonon vertex. Time runs in the vertical direction.

An alternative explanation for the Raman peak near $2\omega_0$ was suggested by Tubino and Birman,[8] who proposed on the basis of a Keating-type force-constant model that the phonon dispersion does not have its maximum at Γ, but rather somewhere along the (100) or Δ direction of the LO branch. A Raman peak originating from the saddle-point van-Hove singularity at Γ would then occur at $2\omega_0$. Our *ab initio* frozen-phonon calculations support this model. We have calculated the dispersion of the LO-LA branch at $q/X=0$, $\frac{1}{3}$, $\frac{2}{3}$, and 1, using a twelve-atom supercell geometry. Assuming that the interplanar harmonic coupling constants can be trucated beyond sixth neighbor, we can obtain the entire dispersion curve along Δ; the maximum, which is indeed displaced from Γ, has a value 6.8 cm^{-1} above ω_0. Unfortunately, in the Tubino-Birman model the peak is pinned at exactly $2\omega_0$; thus the experimentally observed Raman shift above $2\omega_0$ remains puzzling.

The fact that the calculated ω_0 is too high by ~ 12 cm^{-1} compared to experiment may be due in part to the fact that only the bare frequencies have been calculated. We can go one step further and calculate the self-energy correction due to diagrams of the kind shown in Fig. 3. There is now no requirement that $\vec{k}$ be small for the internal lines, but if we make the assumptions (13) anyway and use the values of Eq. (15), we obtain

$$\Delta\omega \approx \frac{3\hbar}{4M^2\omega_0^2}(\alpha+2\beta') = -17.4\ \mathrm{cm}^{-1}. \qquad (16)$$

This is the correct order of magnitude for the needed correction.

In summary, we have shown that frozen-phonon calculations can be used to determine bare phonon-phonon scattering amplitudes, and that consideration of virtual processes allows renormalized multiphonon vertices and phonon self-energies to be calculated as well. The renormalized four-phonon vertices are found to be negative for optical zone-center phonons in diamond, implying that the two-phonon bound state cannot form. It appears that this approach can be extended to compute other quantities such as decay lifetimes and even thermodynamic properties, given a sufficiently systematic treatment along the lines illustrated here.

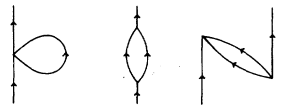

FIG. 3. Feynman diagrams representing the contribution of three- and four-phonon processes to the renormalization of the phonon self-energy.

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[13]We have calculated $\Phi_{x,x,x,x}(\vec{k},\vec{k},-\vec{k},-\vec{k})$ for a few points along $\hat{k} \parallel (100)$; the results support this assertion.

[14]We have omitted the effect of virtual acoustical-phonon exchange, which would presumably make the renormalized fourth-order coupling even more negative.