RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 43, NUMBER 5 15 FEBRUARY 1991-I

Anharmonic self-energies of phonons in silicon

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(Received 21 September 1990)

We have carried out a realistic *ab initio* calculation of the contribution of cubic anharmonicity to the inverse lifetime Γ and the frequency shift Δ of phonons in silicon. The cubic coupling constants for phonons throughout the Brillouin zone are obtained from an anharmonic Keating-type lattice-dynamical model, which has been fit to a database of results from local-density-approximation frozen-phonon and elastic-modulus calculations. Γ and Δ have been calculated as a function of temperature T and wave vector. Our results agree reasonably well with experiment, but indicate the need for retention of quartic and higher-order terms, especially at high T.

Until recently, our understanding of anharmonic effects in solids has been rather incomplete. Though the *formalism* for the perturbation expansion of the phonon propagator was worked out long ago,[1] knowledge about *phonon-phonon interactions in real solids* has been lacking, especially for optical phonons. The anharmonic sector has typically been described by simple models with one or two parameters[2,3] that have been fit to empirical data such as measured anharmonic elastic constants or coefficients of thermal expansion. Thus, realistic calculations of anharmonic effects, such as phonon decay rates and frequency shifts, have not been possible.

In this paper, we describe a completely-first-principles calculation of the leading contribution from cubic anharmonicity to phonon lifetimes and frequency shifts in a crystal. Using silicon as a prototype, we have implemented a three-part strategy. First, frozen-phonon total-energy and force calculations have been carried out within the local-density approximation (LDA), providing values for anharmonic multiphonon coupling constants. Since such frozen-phonon calculations are computationally feasible only for supercells of moderate size, anharmonic coupling constants are easily obtained only for phonons at a correspondingly small number of points in the Brillouin zone (BZ). Therefore, the second part of our strategy is to introduce an anharmonic lattice-dynamical model which is used to obtain the anharmonic couplings at arbitrary k points by interpolation. Finally, this model is used to carry out the BZ integrations needed to evaluate the phonon lifetimes and frequency shifts.

Specifically, LDA pseudopotential calculations have been carried out for the homogeneously strained crystal[4] and for frozen phonons at the Γ point[4,5] and X point.[6] Theoretical values for twelve distinct cubic coupling constants have thus been extracted (e.g., cubic elastic constants, mode Grüneisen parameters, and purely optical three-phonon interactions). A six-parameter, cubic anharmonic model of the Keating type,[7] which systematically includes all two- and three-body interactions of nearest-neighbor triplets of atoms, provides a very successful fit to this database of twelve cubic constants.[6] (The model has another six parameters which describe the harmonic sector, as in the work of Tubino, Piseri, and Zerbi.[8] These provide accurate phonon-dispersion relations and eigenvectors.)

The frequency shift Δ and the inverse lifetime Γ of a phonon $(\mathbf{k},\lambda)$ are given by the real and imaginary parts, respectively, of the phonon self-energy $\Sigma(\mathbf{k},\lambda;\omega)$, evaluated at the phonon frequency $\omega_{\mathbf{k},\lambda}$; these quantities can be measured by Raman-scattering experiments. 2Γ is essentially the linewidth of the Raman line, while Δ gives the shift in the position of the line center. Figure 1(a) represents the lowest-order contribution to the phonon self-energy when we restrict ourselves to diagrams with three-phonon vertices only. The contribution to the inverse lifetime, at temperature T, from this diagram is given by[1]

$$\Gamma(\mathbf{k},\lambda;\omega)=\frac{18\pi}{\hbar^2}\sum_{\mathbf{k}_1}\sum_{\lambda_1,\lambda_2}|V(-\mathbf{k},\lambda;\mathbf{k}_1,\lambda_1;\mathbf{k}_2,\lambda_2)|^2\{(n_1+n_2+1)[\delta(\omega-\omega_1-\omega_2)-\delta(\omega+\omega_1+\omega_2)]$$
$$+(n_1-n_2)[\delta(\omega+\omega_1-\omega_2)-\delta(\omega-\omega_1+\omega_2)]\}\,, \tag{1}$$

where we have employed the shorthand notation $\omega_i \equiv \omega_{\mathbf{k}_i,\lambda_i}$, and n_i is the corresponding Bose-Einstein occupation factor. The interaction between three phonons $(\mathbf{k}_1,\lambda_1)$, $(\mathbf{k}_2,\lambda_2)$, and $(\mathbf{k}_3,\lambda_3)$ is given by the matrix element $V(\mathbf{k}_1,\lambda_1;\mathbf{k}_2,\lambda_2;\mathbf{k}_3,\lambda_3)$; it is basically the third derivative of the potential energy with respect to normal-mode coordinates.

Experimental measurements of the phonon lifetimes

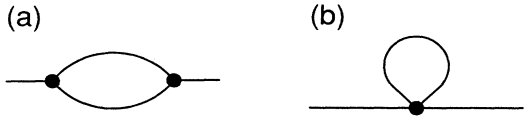

FIG. 1. Feynman diagrams for the lowest-order contributions to the phonon self-energy from (a) cubic interactions and (b) quartic interactions.

have focused on the Raman-active mode at the zone center;[9-11] we therefore consider its anharmonic properties in detail. By merely using conservation of energy and momentum, we find that the zone-center optical phonon can decay only into pairs of phonons (of opposite wave vector) which lie in the bands 2-3, 1-3, 3-3, and 2-2, where the bands are numbered in order of increasing energy. All four possibilities involve *pairs of acoustic phonons only,* in contradiction to a previous assertion[11] that the dominant decay channel involves pairs of LA-LO phonons. We further find that most of the final-state phonons lie near the edges of the BZ.

The inverse lifetime given by Eq. (1) was evaluated by summing over a grid corresponding to 23328 k points in the BZ. We used the Gaussian form of the δ function,

$$\delta(\omega)=\lim_{\varepsilon\to 0}(\sqrt{\pi\varepsilon})^{-1}\exp(-\omega^2/\varepsilon)\,, \tag{2}$$

with $\varepsilon=150$ cm^{-2} for pairs of acoustic bands and $\varepsilon=75$ cm^{-2} for the remaining combinations. Making use of the fact that the matrix elements $V(-\mathbf{k},\lambda;\mathbf{k}_1,\lambda_1;\mathbf{k}_2,\lambda_2)$ vary fairly smoothly along the BZ, we evaluated these only on a coarser grid corresponding to 2916 k points, thus saving on computational time.

In Figs. 2(a) and 2(b), we show the frequency dependence of the two-phonon density of states $D_2(\omega)$ and the inverse lifetime $\Gamma(0,\lambda;\omega)$. The striking difference between the shapes of the two curves illustrates the strong dependence of the matrix elements on wave vector, and serves to emphasize the importance of having a realistic model for the cubic interactions.

Figure 3(a) shows our results for the variation of 2Γ as a function of temperature T, for the zone-center optical phonon. Our value of $2\Gamma(0)=0.48$ cm^{-1} may be compared with experimental values of 1.40 (Ref. 8) and 1.24 cm^{-1} (Ref. 9). We regard this as reasonably good agreement, considering that the theory is entirely free of empirical parameters, and that we have neglected quartic and higher-order anharmonic terms, which may be significant even at low T. (Although the matrix elements for decays involving four or more phonons may be small, the amount of phase space occupied by allowed final states is much larger than in the cubic case.) We find that 65% of the decay rate at $T=0$ comes from decays to bands 2 and 3, and 31% from bands 1 and 3. This shows that the Klemens approximation[12] (that the zone-center optical-phonon decays only to two phonons in band three, each at half the frequency) is completely unjustified. The agreement with experiment worsens as T increases; this is almost certainly because the relative magnitude of the neglected quartic and higher-order anharmonic terms increases with T. This conclusion is supported by an examination of the T dependence of the experimental points.[10] At high T, the contribution to the self-energy from the cubic interactions at second order [Fig. 1(a)] is linear in T, while the contribution from cubic interactions at fourth order and quartic interactions at second order (which we have neglected) varies quadratically with T.

We have also calculated the cubic contribution to Γ for all the phonon branches at the X and L points in the BZ, as a function of T. These results are shown in Figs. 3(b) and 3(c). We are not aware of the existence of any experimental data to which these results can be compared. (A different grid in k space, corresponding to summing over

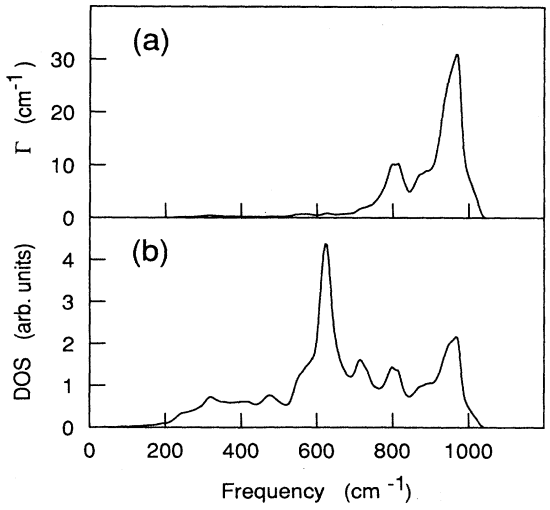

FIG. 2. Frequency dependence of (a) two-phonon density of states $D_2(\omega)$ and (b) inverse lifetime $\Gamma(0,\lambda;\omega)$, for decay of the zone-center optical phonon, at zero temperature.

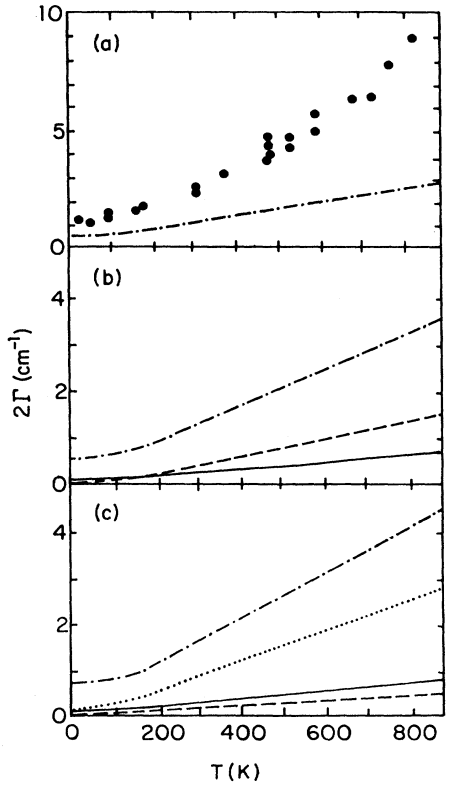

FIG. 3. 2Γ as a function of absolute temperature T, at the (a) Γ, (b) X, and (c) L points. The large dots in (a) are the experimental points from Ref. 11. The lines are results of the present work: dashed lines, TA modes; solid lines, LO modes; dotted lines, LA modes; dash-dotted lines, TO modes.

11 200 points in the BZ was used for the calculations at the L point.) Figure 4 shows our results for 2Γ as a function of $\mathbf{k}$ for optical phonons along the [100] direction, at $T=0$. We find that most of the variation in Γ along the BZ is due to variations in matrix elements, and not merely due to phase-space factors.

The contribution of the diagram of Fig. 1(a) to the frequency shift was computed by utilizing the Kramers-Krönig relation:

$$\Delta(\mathbf{k},\lambda;\omega)=-\frac{1}{\pi}\int_{-\infty}^{+\infty}\frac{\Gamma(\mathbf{k},\lambda;\omega')d\omega'}{\omega'-\omega}. \quad (3)$$

There is an additional contribution to the frequency shift from the thermal expansion of the crystal. At temperature T, this is given by[13]

$$\Delta^{E}(\mathbf{k},\lambda)=\omega_0\left[\exp\left(-3\gamma\int_0^T\alpha(T')dT'\right)-1\right], \quad (4)$$

where ω_0 is the phonon frequency at $T=0$, γ is the mode-Grüneisen parameter,[14] and $\alpha(T')$ is the coefficient of thermal expansion at temperature T'.[15]

Our results for $\Delta(T)-\Delta(0)$ as a function of T, for optical phonons at the Γ, X, and L points, are depicted in Figs. 5(a)–5(c). Unlike the lifetimes, the frequency shifts have been measured experimentally not just at the zone center, but also at the X and L points.[16] It can be seen that the agreement with experiment is, on the whole, quite reasonable. However, it should be noted that we have not included a term that occurs at the same order in perturbation theory as the diagram of Fig. 1(a); this is the first-order quartic term corresponding to the diagram of Fig. 1(b). Since this term contributes to the frequency shift (but not to the lifetime), our results for Δ may be altered significantly upon the inclusion of quartic interactions. Further, this first-order quartic contribution to Δ could be either positive or negative in sign. We attempted to calculate this term by utilizing the quartic sector of the lattice-dynamical model described in Ref. 6. However, we found that this part of the model was not sufficiently constrained, making our results for the quartic terms unreliable. Future LDA calculations could be used to improve this sector of the model and thus obtain the entire frequency shift to leading order.

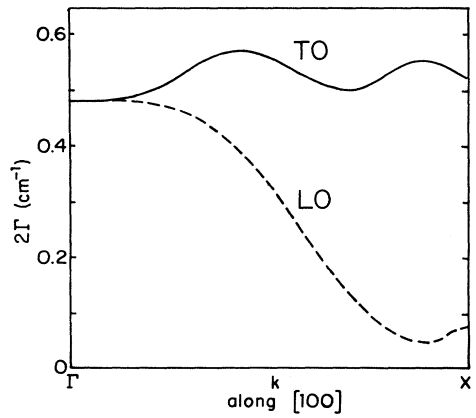

FIG. 4. Theoretically calculated values of 2Γ as a function of $\mathbf{k}$ along the [100] direction, for the optical modes at $T=0$.

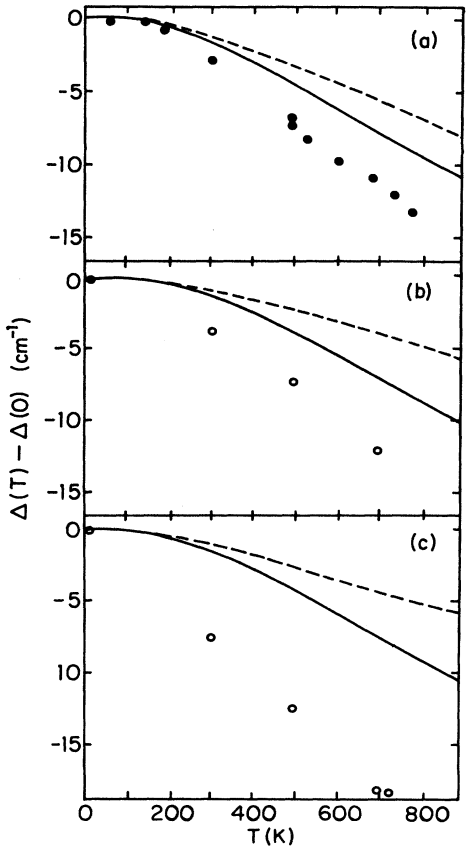

FIG. 5. Temperature dependence of the frequency shift Δ, for (a) LTO at Γ, (b) TO at X, and (c) TO at L. The dashed lines are the theoretical contribution from cubic anharmonicity alone, the solid lines include the effects of thermal expansion. The dots and open circles are the experimental points from Refs. 11 and 16, respectively.

We find that the frequency shift for the TA modes is very small, e.g., $\Delta=-0.26\ \mathrm{cm}^{-1}$ at the X point. The TA bands along Γ to X are unusually flat near the zone edges; this has usually been attributed to the presence of long-range Coulomb interactions.[17] Our work eliminates the alternative possibility that this may be caused by an anomalously large contribution to the frequency shift from Fig. 1(a).

As has been discussed above, a large part of the discrepancy with experiment is probably due to the neglect of higher-order anharmonic terms, which may be particularly important when computing the frequency shift. (In principle, we have all the information needed to include cubic terms at higher order, but such calculations are extremely tedious, and would remain incomplete unless we could include quartic interactions on the same footing.) It is also possible that some of the discrepancy may be due to shortcomings in the lattice-dynamical model, even though the fit in the cubic sector is quite good.[6]

Finally, we note that an alternative approach has been used recently by Wang, Chan, and Ho, who extracted in-

formation about anharmonic effects from molecular-dynamics simulations.[18] Since the dynamics of the particles was treated classically, their results are strictly valid only at high temperatures. Thus, their work is in some sense complementary to ours, since our results are better at low temperatures where higher-order anharmonic terms are less important.

In summary, we have used information from LDA calculations to compute the contribution from cubic interactions to phonon lifetimes and frequency shifts in silicon. The agreement with experiment is fairly good, though it appears that quartic and higher-order terms are important, especially at high temperatures. Our results reveal considerable complexity in the contributions from various k points and band combinations, indicating that the kinds of simple approximations used in previous calculations[2,3,12] are inadequate. They also clear up previous confusion about the allowed channels for decay of the zone-center optical phonon, and show no evidence of significant anharmonic contributions to the softening of the TA modes at X. Finally, and most importantly, our calculations demonstrate the feasibility of carrying out completely-first-principles computations of anharmonic effects.

This work was supported by NSF Grant No. DMR-88-17291. One of us (D.V.) wishes to acknowledge additional support from the Alfred P. Sloan Foundation.

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