

Lifetime of Phonons in Semiconductors under Pressure

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We have measured the pressure dependence of the width of the first-order Raman lines in Si and Ge at low temperature. The width increases linearly with hydrostatic pressure, which implies a decrease of the lifetime of the long-wavelength optical phonons. The results are compared with recent first-principles calculations of anharmonic decay into two phonons of lower energy, based on third-order density-functional perturbation theory. Provided the calculations are slightly adjusted so that the relevant frequencies agree *exactly* with the measured ones, the agreement for the linewidths between theory and experiment is excellent. [S0031-9007(97)02433-2]

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The homogeneous width of first-order Raman lines is an important physical parameter, as it reflects anharmonic interactions of the Raman-active optical phonons causing their decay into combinations of phonons of lower energy. Such decay determines the lifetime of nonequilibrium phonons usually probed by time-resolved spectroscopy. The full width at half maximum (FWHM, Γ) of Raman lines has been measured repeatedly in the past for various materials, particularly for diamond-type crystals [1]. The measurements include the temperature (T) dependence of Γ and of the optical phonon frequency ω_R . The T dependence of Γ is governed by changes in phonon occupation numbers. On the other hand, the dependence of Γ on hydrostatic pressure (P) is expected to reveal the influence of the phonon dispersion on decay processes, due to changes in phonon frequencies throughout the Brillouin zone. Data on the phonon FWHM vs P are not available, with the exception of early work on GaP at 300 K [2].

In this Letter we report measurements of the FWHM of optical phonons in Si and Ge for pressures $P \leq 9.2$ GPa at low temperature (6 K). The present experiments revealed zero-pressure linewidths smaller than all previous experimental values. We observe that in both cases the FWHM increases linearly under pressure. We compare our results with recent *first-principles* calculations [3] and show that in order to reproduce the experimental data for $\Gamma(P)$, the calculations for Si have to be slightly adjusted so that all relevant phonon frequencies are brought to coincidence with the measured ones.

Different experimental conditions and methods of numerical analysis used by different authors have led to considerable discrepancies in the T -dependent data for $\Gamma(P)$ [1]. Discrepancies exist also in the results of various theoretical works, mostly semiempirical, due to the different models used. A critical review has been presented in Ref. [1]. Several articles have been published ever since where the theoretical results [3–8] appear to converge towards the most recent and most reliable experimental values for ω_R , Γ , and their T dependence. The

work in Ref. [3], in particular, has shown that through *parameter-free* calculations based on third-order density-functional perturbation theory it is possible to reach reasonable agreement between theory and experiment for Γ in Si, Ge, and diamond at ambient pressure. Only three-phonon processes were found to be necessary. At zero pressure, energy conservation allows the zone-center optical phonons to decay into only acoustical branches, the most relevant modes being TA and LA near the zone boundary.

In order to simulate the effect of P on Γ , the authors of Ref. [3] performed their calculations for different crystal volumes. According to these results, as P increases from 1 atm to 10 GPa, the FWHM for Si increases by more than a factor of 2, for Ge by $\sim 50\%$, while for diamond it remains almost unchanged. The variation with P is linear for Ge, whereas Si shows a linear region up to ~ 7 GPa, after which Γ exhibits a change in slope. The linear slopes obtained from the present experiments are nearly equal to the initial ones computed in Ref. [3]. However, we have no evidence of nonlinear regions in Si. We discuss the extent of validity of the theoretical approach of Ref. [3], and suggest refinements based on supplementary density-functional calculations.

The experiments were performed at 6 K in backscattering geometry. Commercial (100)-oriented samples of high purity were mechanically polished to a thickness of 100 μm , and then etched down to ~ 25 μm by immersing Si for 8 min in $\text{CH}_3\text{COOH}(96\%) : \text{HNO}_3(65\%) : \text{HF}(49\%)$ (volume ratio 5:15:2), and Ge for 2 min in $\text{HNO}_3(65\%) : \text{HF}(49\%)$ (3:1). The pressure was applied using a diamond anvil cell with helium as pressure transmitting medium. In order to ensure fully hydrostatic conditions, the cell was heated to a temperature above the melting line of He each time before changing the pressure, and then cooled to 6 K for the next measurement. The pressure was measured to within ± 0.03 GPa using the ruby luminescence method [9] with temperature corrections according to Ref. [10]. The maximum pressure applied was kept below 9.2 GPa in order to avoid possible

defect formation related to structural phase transitions in Si and Ge above 10 GPa.

The 647.1 nm line of a Kr⁺ ion laser was used for excitation at low power densities (200 W/cm²) to avoid sample heating. The scattered light was analyzed by a JY T64000 triple spectrometer in the additive dispersion mode using single-channel photon counting. The entrance and exit slits were kept at 200 μm (150 μm) for Si (Ge), corresponding to an instrumental resolution of 1.15 cm⁻¹ (0.9 cm⁻¹). For each Raman spectrum, an additional spectrum of a nearby Ne line was measured, in order to check the exact values of the resolution as well as the phonon frequency ω_R . The spectrometer profile corresponded to a Gaussian line shape. The incident light was always polarized parallel to the spectrometer slits. For backscattering along [100], only LO phonons participate, and the scattered light is polarized perpendicularly to the slits. Our tests showed substantial deviation from the Raman selection rules, partly because of polarization scrambling by the diamond windows. The spectral profiles, however, were independent of the analyzer orientation. Therefore, the spectra were taken mainly without analyzer.

The Raman intensity observed for Si decreased by a factor of ~ 3 at 9 GPa due to increased absorption. In Ge, the intensity also decreased slightly with increasing pressure, but above 8 GPa it increased by at least an order of magnitude, owing to the *P*-shifted E_0 gap which at 9 GPa coincides [11] with the excitation energy of 1.916 eV.

Figure 1 shows Raman spectra of Ge at zero pressure and near 9 GPa. The observed line shape corresponds to the convolution of a true Lorentzian with the Gaussian instrumental profile. The result of this convolution is known as the Voigt profile [12]. The FWHM of the Lorentzian component (Γ) was obtained by fitting a Voigt profile to the experimental data using a fixed width for the Gaussian component, as obtained from the Ne line spectrum. The Lorentzian width found in this way was tested with various slit widths at fixed pressure. Within error (± 0.05 cm⁻¹ for Si, ± 0.07 cm⁻¹ for Ge) the FWHM was independent of the slit width.

Figures 2 and 3 show ω_R and Γ , respectively, as a function of *P*, both for increasing and decreasing pressure. The results were fully reversible, and the zero-pressure spectra before and after the pressure cycle were identical. The error bars correspond to the statistical distribution of at least six measurements at each pressure. Solid lines represent least squares fits of quadratic (linear) functions to the data for ω_R (Γ). The relations for ω_R (6 K, *P*) are, in cm⁻¹,

$$\omega_R^{\text{Si}}(P) = 523.88(10) + 5.10(4)P - 0.062(4)P^2, \quad (1)$$

$$\omega_R^{\text{Ge}}(P) = 304.64(13) + 4.02(7)P - 0.059(8)P^2, \quad (2)$$

where *P* is in GPa. Within error, the pressure coefficients in Eq. (1) agree with those of Ref. [13] at 300 K. Using

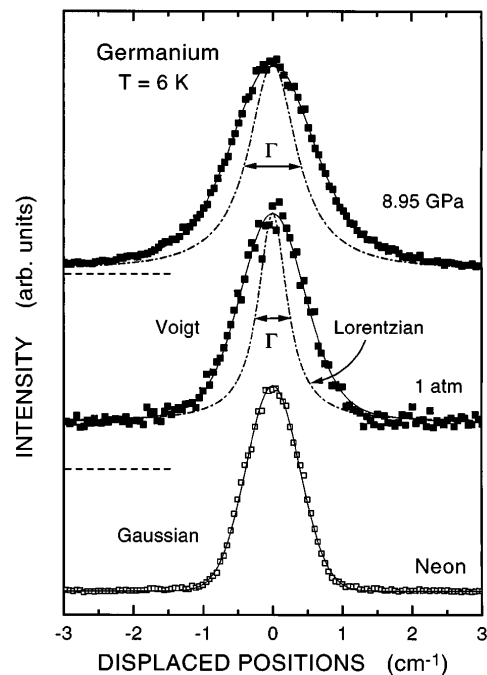


FIG. 1. Normalized Raman spectra of Ge at 6 K under ambient and high pressure, measured with 647.1 nm excitation. The dash-dotted curves correspond to the computed true Raman lines (Lorentzian) obtained from Voigt profiles fitted to the experimental data. The Ne calibration line was used to determine the spectrometer response function. For clarity, the spectra have been displaced along the frequency axis.

the bulk modulus $B_{\text{Si}}(6 \text{ K}) \approx 99 \text{ GPa}$ [14], we obtain a mode Grüneisen parameter of $\gamma_{\text{Si}}(6 \text{ K}) = 0.96(1)$, which is nearly the same as $\gamma_{\text{Si}}(300 \text{ K}) = 0.98(6)$ [13]. For Ge we find $\gamma_{\text{Ge}}(6 \text{ K}) = 1.00(1)$ using $B_{\text{Ge}}(4 \text{ K}) = 75.8 \text{ GPa}$ [15], as compared to $\gamma_{\text{Ge}}(300 \text{ K}) = 1.12(2)$ given in Ref. [16].

The dash-dotted lines in Fig. 2 correspond to our calculations based on the model of Ref. [3]. For Ge, the agreement is excellent. In Si, we find a parallel downward shift of $\sim 15 \text{ cm}^{-1}$ or 3%, and this indicates limitations of the model, which will be discussed below.

Next we consider the *P* dependence of Γ (Fig. 3). The fitted linear relations for $\Gamma(6 \text{ K}, P)$ are, in cm⁻¹,

$$\Gamma_{\text{Si}}(P) = 1.08(5) + 0.137(2)P, \quad (3)$$

$$\Gamma_{\text{Ge}}(P) = 0.51(7) + 0.037(3)P. \quad (4)$$

Neither of these pressure coefficients has been measured before. Also, the zero-pressure linewidths are smaller than all experimental values reported previously. Compared to the results of Menéndez *et al.* [1,17] we believe this is due mainly to the chemical etching of our samples. Fuchs *et al.* [18] found, for natural Ge, $\Gamma = 0.89(2) \text{ cm}^{-1}$ using the 514.5 nm laser line, a result which we reproduced when we used the same laser line. We have actually found systematically larger linewidths in Ge

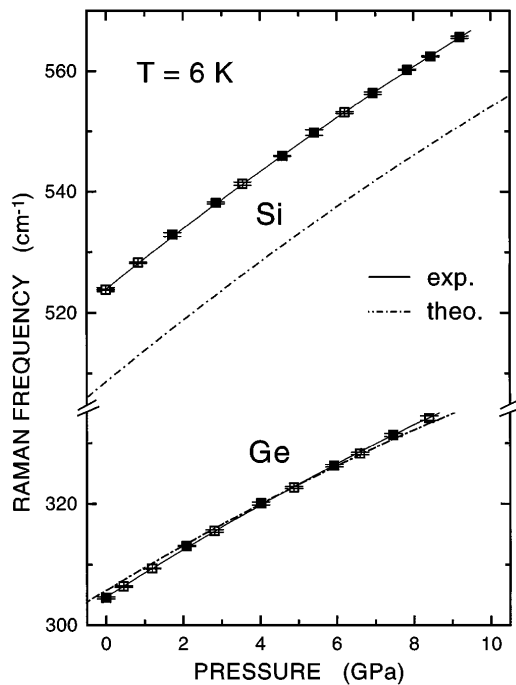


FIG. 2. Optical phonon frequencies for Si and Ge, measured for increasing (filled squares) and decreasing (open squares) pressure. The solid lines correspond to the fitted relations Eqs. (1) and (2) for Si and Ge, respectively. The dash-dotted lines represent the results of the present calculations.

for excitations near ≈ 500 nm. This can be attributed to the very small light penetration depth (< 20 nm) at these wavelengths, resulting in both a sampling of Raman scattering from a larger \mathbf{k} -vector region near the zone center and a higher sensitivity to strains in the surface region.

The dashed curves in Fig. 3 represent the calculated Raman linewidths of Ref. [3] versus calculated pressure. In the case of Ge the agreement can be considered excellent, taking into account the fact that the higher-order anharmonic force constants were calculated from first principles. The FWHM for Si, apart from a parallel shift, shows a noticeable nonlinearity at ~ 7 GPa. According to Ref. [3], no new decay channels are activated in Si at low pressures, and the function $\Gamma(P)$ should be nearly linear. At higher pressures new channels, e.g., LO + TA, are predicted to become allowed, causing the change in slope of the calculated $\Gamma(P)$ at ~ 7 GPa [3]. Our data for Si do not show any such nonlinearity and, within error, evolve quasilinearly in the entire range of pressure; this means that the new decay channels involving an optical branch do not actually participate in the decay process.

We believe that the parameter-free calculation of Ref. [3] is more realistic than all previous models, while nevertheless being susceptible to refinements. The nonlinearity of $\Gamma(P)$ in Si calculated at ~ 7 GPa is a consequence of the differences between computed and experimental phonon frequencies. At $P = 0$ the computed value of ω_R is lower in frequency by 15 cm^{-1}

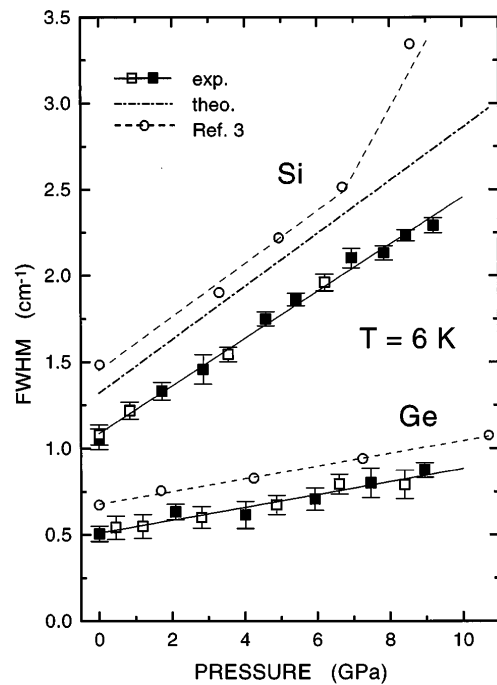


FIG. 3. Pressure dependence of the full width at half maximum of the Raman lines in Si and Ge. Filled and open squares refer to increasing and decreasing pressure, respectively. The solid lines represent the fitted Eqs. (3) and (4). The dashed lines are calculated results from Ref. [3]. The dash-dotted line represents the results of the present calculation for Si.

compared to the experimental one (see Fig. 2). Such discrepancies are different for other phonon modes such as those into which the Γ phonons decay; the error in the frequency of the LO + TA phonon sum mentioned above is 20 cm^{-1} . The equation used in Ref. [3] for Γ , assuming three-phonon processes and energy-momentum conservation, is written in the simplified form

$$\Gamma(\omega_R) = \frac{b}{\omega_R} \sum_{\mathbf{q}, i, j} f(\mathbf{q}, i, j) \delta(\omega_R - \omega_{i\mathbf{q}} - \omega_{j\bar{\mathbf{q}}}), \quad (5)$$

where b is a constant, $i, j = 1 - 6$ are branch indices, and $f(\mathbf{q}, i, j)$ is a function of phonon amplitudes and frequencies ($\omega_{i\mathbf{q}}$ from all over the Brillouin zone). To check the sensitivity of $\Gamma(\omega_R)$ to different choices of ω_R , we have evaluated Eq. (5) as a function of ω_R in the region of the experimental values of $\omega_R(P)$. The results are shown in Fig. 4 by dashed lines. The dashed and solid vertical lines indicate the computed and experimental values of ω_R , respectively.

For $P = 0$, the function $\Gamma(\omega_R)$ exhibits three quasilinear regions, AB , BC , and CD of different slopes. The region BC is due to the activation of the decay pair LO + TA mainly around the L point, with frequency for LO + TA at L (point B) of $\sim 515 \text{ cm}^{-1}$ [3]. According to neutron scattering [19] this sum should be $\sim 535 \text{ cm}^{-1}$ at 6 K, i.e., 20 cm^{-1} higher in frequency than point B . This suggests to shift the entire curve AD to

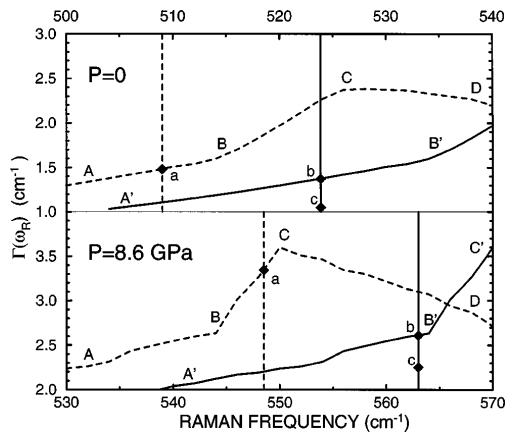


FIG. 4. The FWHM of the Raman line of Si as a function of phonon frequency ω_R at zero pressure and at 8.6 GPa. The dashed curves represent the computed results based on the model of Ref. [3]. Solid curves are obtained by rigidly shifting the dashed ones (see text). Vertical dashed (solid) line: computed [3] (present experimental) ω_R . For $P \neq 0$, the crossing point b lies in the linear region $A'B'$.

higher frequency by 20 cm^{-1} (solid curve). At the experimental frequency 524 cm^{-1} (point b) we then find $\Gamma_b = 1.35 \text{ cm}^{-1}$, a width closer to the experimental value Γ_c than the calculated (unshifted) value Γ_a .

The same procedure (a 20 cm^{-1} rigid shift) is now applied to the dashed curve for $P = 8.6 \text{ GPa}$, assuming that the theory represents correctly the pressure shifts. The new crossing point b lies in the linear region $A'B'$; furthermore Γ_b is closer to Γ_c than the calculated (unshifted) value Γ_a . Combining the facts that (i) $\Gamma(\omega_R)$ is linear in ω_R in the region $A'B'$, (ii) $\omega_R(P)$ is nearly linear in P in the same region (Fig. 2), and (iii) the point b lies in $A'B'$, we conclude that in the region 0 to 8.6 GPa the function $\Gamma(P)$ should be linear, in contrast with Ref. [3] and in agreement with the present experimental results. The same arguments hold for other values of P in the region from 7 to 10 GPa, where the nonlinearities of Ref. [3] are developed.

In conclusion, we have shown that the measured Raman linewidths of Si and Ge depend linearly on hydrostatic pressure. The decrease of the phonon lifetime with increasing pressure is attributed to pressure-induced changes in the density of final states of the two-phonon spectrum governing the anharmonic decay. We have also demonstrated that density-functional perturbation theory offers a realistic basis for *ab initio* calculations of the anharmonic phonon decay, provided its details are rigorously tested against all available experimental information. It is unlikely that an experiment with diamond would produce any measurable changes in the FWHM;

under *hydrostatic* conditions such effects are expected beyond 100 GPa [3], presently impossible to attain through conventional diamond-anvil cells. However, differences in the phonon decay mechanisms of LO and TO modes in III-V crystals under pressure, as well as pressure effects on the line shapes of second-order Raman spectra, may help to further elucidate the physical picture of phonon lifetimes in semiconductors.

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- [1] J. Menéndez and M. Cardona, Phys. Rev. B **29**, 2051 (1984), and references therein.
- [2] B. A. Weinstein, Solid State Commun. **20**, 999 (1976).
- [3] A. Debernardi, S. Baroni, and E. Molinari, Phys. Rev. Lett. **75**, 1819 (1995).
- [4] E. Haro, M. Balkanski, R.F. Wallis, and K.H. Wanser, Phys. Rev. B **34**, 5358 (1986).
- [5] C.Z. Wang, C.T. Chan, and K.M. Ho, Phys. Rev. B **40**, 3390 (1989).
- [6] S. Narasimhan and D. Vanderbilt, Phys. Rev. B **43**, 4541 (1991).
- [7] S. Konval and R. Migoni, Phys. Rev. B **49**, 998 (1994).
- [8] E. Haro-Poniatowski, J.L. Escamilla-Reyes, and K.H. Wanser, Phys. Rev. B **53**, 12 121 (1996).
- [9] G.J. Piermarini, S. Block, J.P. Barnett, and R.A. Forman, J. Appl. Phys. **46**, 2774 (1975); H.K. Mao, J. Xu, and P.M. Bell, J. Geophys. Res. **91**, 4673 (1986).
- [10] S. Buchsbaum, R.L. Mills, and D. Schiferl, J. Phys. Chem. **88**, 2522 (1984).
- [11] G.H. Li, A.R. Goñi, K. Syassen, and M. Cardona, Phys. Rev. B **49**, 8017 (1994).
- [12] D.W. Posener, Aust. J. Phys. **12**, 184 (1959).
- [13] B.A. Weinstein and G.J. Piermarini, Phys. Rev. B **12**, 1172 (1975).
- [14] J.J. Hall, Phys. Rev. **161**, 756 (1967).
- [15] L.J. Bruner and R.W. Keyes, Phys. Rev. Lett. **7**, 55 (1961).
- [16] C.J. Buchenauer, F. Cerdeira, and M. Cardona, in *Light Scattering in Solids*, edited by M. Balkanski (Flammarion, Paris, 1971), p. 280.
- [17] According to Ref. [1], the measured FWHM for Si and Ge at 0 K are 1.24 ± 0.07 and $0.75 \pm 0.03 \text{ cm}^{-1}$, respectively, using 647.1 nm excitation.
- [18] H.D. Fuchs, C.H. Grein, R.I. Devlen, J. Kuhl, and M. Cardona, Phys. Rev. B **44**, 8633 (1991).
- [19] G. Nilsson and G. Nelin, Phys. Rev. **6**, 3777 (1972).