PHYSICAL REVIEW B VOLUME 1, NUMBER 2 15 JANUARY 1970

Temperature Dependence of Raman Scattering in Silicon

T. R. Hart,* R. L. Aggarwal, and Benjamin Lax*

Francis Bitter National Magnet Laboratory,† Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139

(Received 2 June 1969; revised manuscript received 4 August 1969)

We have measured the linewidth and the frequency of the $\mathbf{q}=0$ optical phonon in silicon over the temperature range of 20–770°K. The temperature dependence of the linewidth has been interpreted as arising from the decay of the optical phonon to two LA phonons at half the optical frequency. From the observed temperature variation, we deduce an absolute half-width Γ of 2.1 cm^{-1} at 0°K. This value is considerably smaller than that obtained theoretically by Cowley on the basis of numerical calculations which include decay to phonons throughout the Brillouin zone. His numerical calculations also predict a temperature dependence of the linewidth which does not agree with experiment. However, the observed change in frequency with temperature correlates very well with Cowley's theory. We have also studied the relative intensities of Stokes and anti-Stokes components of Raman spectra. The observed temperature dependence of the relative intensities is compared with that predicted on the basis of the Bose-Einstein population factor for the optical phonon.

I. INTRODUCTION

THE class of diamond structure crystals provides a simple system in which anharmonic crystal theory can be tested against experiment. Extensive neutron data on the phonon dispersion curves in diamond, silicon, and germanium have permitted Cowley[1] to make numerical calculations using the theory developed by Kokkedee,[2] and Maradudin and Fein.[3] In anticipation of Raman experiments, Cowley tabulated values for the linewidth and frequency of the optical phonon at 10, 100, 300, and 500°K. The first Raman studies of silicon were made at room temperature by Russell[4] with a He-Ne laser and by Parker *et al.*[5] with specimens located inside the cavity of an argon laser. The experimentally determined linewidth was many times smaller than the value calculated by Cowley.[1] Klemens[6] suggested a modification of the theory whereby the coupling of the optical mode to the acoustic branches was reduced and yielded a smaller estimate for the linewidth in somewhat better agreement with Parker's experiment. We have now measured the temperature dependence of the linewidth and frequency in the temperature range 20–770°K. The experimental results for the change in frequency with temperature are in very good agreement with Cowley's calculations, but the absolute value of the observed linewidth and its temperature dependence are in serious disagreement with his theoretical results. We have successfully interpreted the temperature dependence of the linewidth on the assumption that the lifetime of the zone-edge optical phonon is principally limited by its decay to two LA phonons with energy equal to one-half of that of the optical phonon.[6]

II. EXPERIMENTAL PROCEDURE

The Raman spectra were obtained using the 5145 Å line of a model 52 Coherent Radiation Laboratories argon ion laser equipped with an intracavity prism wavelength selector. The nonlasing fluorescent radiation was eliminated by a narrow bandpass filter with peak transmission at the laser wavelength. We used specimens of web grown silicon with a mirrorlike as-grown (111) face. These provide an excellent surface for reflection experiments since they are free of any mechanical damage which might be introduced in the usual process of specimen preparation. The incident laser radiation was polarized along the $[11\bar{2}]$ direction. Radiation scattered along the $[111]$ direction was collected using $f/1$ optics matched to an $f/7$ Spex double grating monochromator equipped with 600 lines/mm gratings blazed at 1.0 μ. The spectra were recorded in the second order using an S-20 photomultiplier and phase-sensitive electronic detection. The spectra were measured with 200-, 100-, 50- and 30-μ slits. The observed half-widths were then corrected for the instrumental resolution by extrapolation to zero slitwidth.

The low-temperature data were obtained with the specimen in contact with the cold finger of a Dewar with liquid nitrogen or liquid helium as the coolant. To prevent high power densities from locally heating the sample, cylindrical focusing optics were used. The illuminated area is a rectangle approximately 1×0.002 cm, yielding an estimated power density of 200 W/cm^2. Approximately one-half of this radiation is specularly reflected, and a significant amount of the power absorbed by the specimen is reradiated. Thus only a fraction of the incident power is actually converted to heat.

For the high-temperature work above 300°K, an evacuated cell was used. Data were taken for seven

---

[*] Also, Physics Department, Massachusetts Institute of Technology.

[†] Supported by the U. S. Air Force Office of Scientific Research.

[1] R. A. Cowley, J. Phys. (Paris) **26**, 659 (1965).

[2] J. J. Kokkedee, Physica **28**, 374 (1962).

[3] A. A. Maradudin and A. E. Fein, Phys. Rev. **128**, 2589 (1962).

[4] J. P. Russell, Appl. Phys. Letters **6**, 223 (1965).

[5] J. H. Parker, Jr., D. W. Feldman, and M. Ashkin, Phys. Rev. **155**, 712 (1967).

[6] P. G. Klemens, Phys. Rev. **148**, 845 (1966).

temperatures in the range 20–770°K. For each temperature approximately ten spectra were recorded and mean values of the observed linewidth and frequency have been used in our analysis.

III. RESULTS AND DISCUSSION

In Fig. 1, we show typical spectra for three temperatures, i.e., 20, 460, and 770°K, observed with 100-μ slits. An integration time of 1 sec gives a signal to noise of approximately 300:1. The change in linewidth, shift in frequency, and change in amplitude are clearly evident. Uncontrolled changes in geometry in going from temperature to temperature vitiate absolute intensity measurements, but we have analyzed the relative amplitudes between Stokes and anti-Stokes components corresponding to the creation and annihilation of an optical phonon.

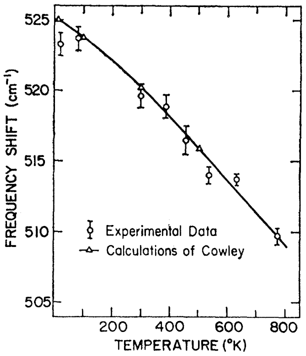

FIG. 2. Frequency shift of the Stokes line versus temperature. The circles represent the experimental points. The triangles represent the frequency shift as calculated by Cowley (Ref. 1) at $T=10$, 100, 300, and 500°K relative to the optical-phonon frequency of 525 cm^{-1} at $T=0$°K. The solid line is the smooth curve drawn through the calculated points with linear extrapolation to 800°K.

A. Frequency Shift

The optical-mode frequency corresponds to a Debye temperature of 740°K. Consequently, the occupation number for the equivalent harmonic oscillator is less than one for our temperature range and we are always in the quantum-mechanical limit of the harmonic oscillator. Even so it is useful to consider the case of a classical anharmonic oscillator. The potential energy is of the form

$$V(x)=cx^2-gx^3-fx^4, \tag{1}$$

where the cubic term gx^3 gives thermal expansion but no change in the frequency to first order. The quartic term fx^4 and the cubic term to second order $(gx^3)^2$ cause a change in the frequency of the modes.[7,8] The relative importance of the terms can be estimated by assuming for the covalent interatomic bond of silicon a Morse potential

$$V(r)=D[(e^{-a(r-r_0)}-1)^2-1], \tag{2}$$

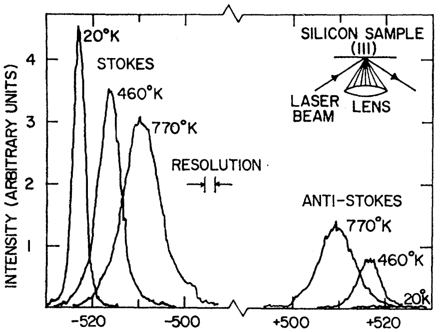

FIG. 1. First-order Raman spectra of silicon observed at 20, 460, and 770°K with an instrumental resolution of ~2 cm^{-1}. Insert shows the scattering geometry used.

where the constants D, a, and r_0 are determined, respectively, by the binding energy of silicon, the stiffness of the bond, and the interatomic spacing. Using the Morse potential to determine the coefficients in the Taylor series expansion for the potential, we find the quartic term is positive, i.e., an increase in frequency, but is only $\frac{3}{5}$ the size of the cubic term to second order, which is negative, and produces a net decrease in frequency.

When we go to the quantum-mechanical calculation each power of x transforms to a creation or an annihilation operator for a phonon, and the frequency shift of the optical mode is calculated as the self-energy of the mode.[2,3] Using these techniques, Cowley[1] has performed a detailed numerical calculation for crystals of the diamond structure using the eigenvectors and eigenfrequencies of harmonic models deduced by fitting the parameters to the phonon dispersion curves obtained by inelastic neutron scattering.[9] The appropriate anharmonic interactions were determined by fitting the experimentally measured thermal expansion.[10]

Our experimentally observed shift in the Stokes component with temperature is compared in Fig. 2 to a solid curve drawn through the value of the shift calculated by Cowley at 10, 100, 300, and 500°K. The overall agreement between experiment and theory is excellent. The data point at the lowest temperature of ~20°K, however, falls well below the theoretical curve, and consistently lower than the value obtained at liquid-nitrogen temperature. It is possible that the above discrepancy is related to the minimum in the Debye temperature of silicon which occurs near 40°K.[10]

---

[7] C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1960), 2nd ed., p. 152.

[8] L. D. Landau and E. M. Lifshitz, *Mechanics* (Addison-Wesley Publishing Co., Inc., Reading, Mass., 1960), pp. 84–87.

[9] G. Dolling, in *Proceedings of International Symposium on the Inelastic Scattering of Neutrons in Solids and Liquids, Vienna, 1962* (International Atomic Energy Agency, Vienna, 1963), Vol. 2, p. 37.

[10] G. Dolling and R. A. Cowley, Proc. Phys. Soc. (London) 88, 463 (1966).

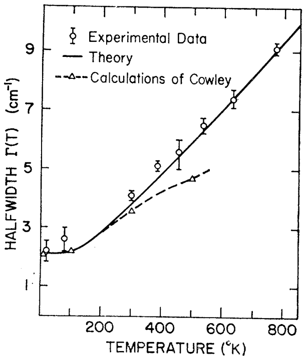

FIG. 3. Plot of the half-width $\Gamma(T)$ for the Stokes component of the first-order Raman line in silicon as a function of temperature. The circles represent the experimental data and the solid line is the theoretical curve obtained from Eq. (6) with $\Gamma(0)=2.1$ cm^{-1}. The dashed line is a smooth curve drawn through the points shown as triangles derived from the numerical calculations of Cowley (Ref. 1).

B. Linewidth

In Fig. 3, we plot the observed half-width, i.e., the full width at half-maxima, of the Stokes component of the first-order Raman line as a function of temperature. The solid line, which gives a good fit to the data, is a theoretical line determined by assuming that the optical-phonon lifetime is limited by decay to two LA phonons of half the frequency. The three-phonon interaction is described by a perturbation Hamiltonian of the form

$$H'=\sum_{\mathbf{q},\mathbf{q}',\mathbf{q}'',\mathbf{x}} e^{i(\mathbf{q}-\mathbf{q}'-\mathbf{q}'')\cdot\mathbf{x}}V(\mathbf{q},\mathbf{q}',\mathbf{q}'')a(\mathbf{q})a^{\dagger}(\mathbf{q}')a^{\dagger}(\mathbf{q}''), \tag{3}$$

where $\mathbf{q}$, $\mathbf{q}'$, and $\mathbf{q}''$ are the wave vectors of the three phonons with frequencies ω, ω', and ω'', respectively. $V(\mathbf{q},\mathbf{q}',\mathbf{q}'')$ is the three-phonon anharmonic coupling coefficient; $a^{\dagger}$ and a are the creation and annihilation operators given by

$$\begin{aligned} a_{N,N+1}{}^{\dagger}&=(\hbar/M\omega)^{1/2}(N+1)^{1/2},\\ a_{N,N-1}&=(\hbar/M\omega)^{1/2}N^{1/2}, \end{aligned} \tag{4}$$

where M is the mass and N is the Bose-Einstein occupation number.

The relaxation rate of a small perturbation n to the thermal equilibrium population N_0 of the optical mode is then proportional to the square of the matrix element of H' between the initial and final phonon states of the system:

$$\begin{aligned} \frac{dn}{dt}&\propto[(N_0+n)(N_a'+1)(N_a''+1)-(N_0+n+1)N_a'N_a'']\\ &\propto n(1+N_a'+N_a'')\\ &\quad+[N_0(N_a'+1)(N_a''+1)-(N_0+1)N_a'N_a''], \end{aligned} \tag{5}$$

where N_a' and N_a'' are acoustic-phonon occupation numbers. The thermal equilibrium part

$$[N_0(N_a'+1)(N_a''+1)-(N_0+1)N_a'N_a'']$$

is zero, since the decay rate of an optical phonon to two acoustic phonons is equal to the recombination rate of the acoustic phonons. Assuming along with Klemens[6] that only the LA phonon contributes, then conservation of momentum and energy require $q_a'=-q_a''$, $\omega_a'=\omega_a''=\frac{1}{2}\omega_0$, and $N_a'=N_a''=N_a$. Expressing N_a in terms of the Bose-Einstein distribution function, the temperature dependence of the half-width Γ obtained from Eq. (5) is

$$\Gamma(T)=\Gamma(0)[1+2/(e^x-1)]. \tag{6}$$

$\Gamma(0)$ is equal to the half-width at $T=0$, and $x=\hbar\omega_0/2KT$, where K is the Boltzmann constant. The solid curve given in Fig. 3 shows the temperature variation of the half-width as obtained from Eq. (6) with $\Gamma(0)=2.1$ cm^{-1}, corresponding to a mean lifetime $\tau=\hbar/\Gamma=2.5\times10^{-12}$ sec.

In Fig. 3, we also show a dashed line drawn through triangles deduced from Cowley's numerical calculations for silicon in the following manner. He calculates for Γ at 10, 100, 300, and 500°K widths of 11.3, 12.0, 19.3, and 29.3 cm^{-1}. To reduce these values to something more in line with experiment, Klemens[6] suggests that the coupling constant which is very nearly temperature-independent over this range has been overestimated for the optical branch. On theoretical grounds Klemens estimates a multiplicative correction factor for the linewidths. We have normalized Cowley's values with a correction factor of 0.186 in order to obtain agreement with the low-temperature data. The deviation of the dashed line from our data in the high-temperature range clearly shows that Cowley's calculation also does not give the correct temperature dependence of the linewidth.

By using $\Gamma(0)$ as an adjustable parameter, we are able to obtain a good fit to the linewidth using decay to two LA modes at half the optical-phonon frequency as the only decay channel. The neutron data of Dolling[9] for the phonon dispersion curves of silicon show that other two phonon decay channels are permitted by conservation of energy and momentum. For example, along the [100] direction an TA and an LA phonon can combine near the zone edge to act as a decay channel for a zone-center optical phonon. All possible decay channels, with their appropriate density of final states, have been included in the numerical calculations given by Cowley. The poor fit of the numerical calculations to the data suggests that there is some additional constraint, other than conservation of energy and momentum, which inhibits these other decay channels.

Before suggesting that changes in anharmonic crystal theory be made, we must note that Dolling and Cowley have successfully used the model to fit several thermodynamic and optical properties of germanium, silicon, diamond, and gallium arsenide. There have been several other experiments related to this problem. Park measured the change in the Raman linewidth in calcite up to 1000°K.[11] He fitted the data using the decay of the 1086-cm^{-1} vibration into a 1085-cm^{-1} plus a 1-cm^{-1} mode. No neutron data is available for the phonon dispersion curves of calcite so no real comparison to theory can be made. Ralston *et al.*[12] have reported some low-temperature linewidth measurements in GaAs and Si obtained with a Nd laser, but have not attempted a theoretical analysis. A more detailed analysis has been done by Pine and Tannenwald[13] in quartz. They studied the linewidth and shift of the 466- and 128-cm^{-1} modes from liquid helium to room temperature. The phonon spectra is very complex, with many optical modes which interact. To fit the linewidth of the 466-cm^{-1} mode, they used three phonon branches and two adjustable parameters. The 128-cm^{-1} mode is even more complicated, involving seven phonon modes and four adjustable parameters.

Clearly, some further experimental work on other systems is suggested, and quite possibly some further theoretical work should be done. Cowley[1] has pointed out that the positive contribution to the line shift Δ due to the quartic term is small and is very nearly canceled by a negative contribution due to the thermal-stress term which is a correction to the frequency due to the change in the volume of the crystal with temperature. If we neglect the canceling contributions of the quartic term and the thermal-stress term, the shift Δ is approximately equal to $\frac{1}{2}\Gamma$, as is evident in Cowley's table for silicon. Our data are not at all consistent with such a simple relationship.

C. Intensity Ratio of Stokes to Anti-Stokes

Another feature of the Raman spectrum is the strong dependence of the intensity of the anti-Stokes line upon temperature. At high temperatures it is of comparable magnitude to the Stokes line but at low temperatures it becomes so weak that it is not observed. In Fig. 4, we compare the observed ratio of intensities of the Stokes and anti-Stokes lines to that predicted by Bose-Einstein statistics. Since the anti-Stokes and Stokes lines correspond, respectively, to the absorption and emission of an optical phonon, the ratio of their intensities I_A and I_S is given by

$$I_A/I_S = N_0/(N_0+1), \tag{7}$$

where N_0 is the equilibrium occupation number of the $\mathbf{q}=0$ optical phonon of frequency ω_0. Since

$$N_0 = [\exp(\hbar\omega_0/KT)-1]^{-1},$$

Eq. (7) simplifies to

$$I_A/I_S = \exp(-\hbar\omega_0/KT). \tag{8}$$

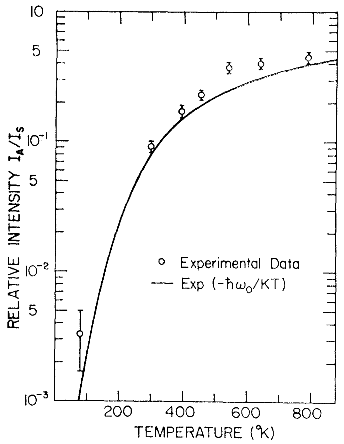

FIG. 4. Plot of the ratio of the intensities for the anti-Stokes to Stokes lines as a function of temperature. The circles show the experimental data, and the solid curve is the function e^{-x}, where $x=\hbar\omega_0/KT$.

The solid curve in Fig. 4 was calculated using experimentally measured ω_0 as a function of temperature (see Fig. 2).

The data points are seen to fall consistently above the theoretical curve. Correction for instrumental response at the two different wavelengths has been made by comparison to a standard tungsten lamp. Heating of the sample by the laser was minimized by keeping the power density low as described in Sec. II. The displacement of the room-temperature point would suggest a heating of 20°K above the ambient temperature; whereas the 630°K point would have to be shifted more than 200°K to make it fall on the theoretical curve. If heating by the laser were a problem, the high-temperature points should have fallen on the curve as it asymptotically flattens off. Since this is not the case, the discrepancy must be principally due to something other than heating of the active volume of the sample, and we cannot use the ratio as a temperature probe as we had initially intended. In addition to undetected systematic errors, there is the possibility that the anti-Stokes component has been enhanced by stimulated emission of optical phonons caused by nonequilibrium population due to the laser beam.

IV. CONCLUSION

In conclusion, we have demonstrated that Raman surface scattering provides a very useful tool for the study of anharmonic properties of crystal vibrations. The temperature dependence of the linewidth for the

---

[11] K. Park, Phys. Letters **25A**, 490 (1967).

[12] J. M. Ralston, D. E. Keating, and R. K. Chang, in *Proceedings of the International Conference on Light Scattering Spectra of Solids, New York, 1968* (Springer-Verlag, Inc., New York, 1969), p. 369.

[13] A. S. Pine and P. E. Tannenwald, Phys. Rev. **178**, 1424 (1969).

zone-center optical phonon in silicon has been explained on the assumption that there is only one decay channel for the optical phonon. This involves the decay into two acoustic phonons at half the optical frequency. But the same model fails to explain the observed temperature dependence of the frequency. This instead correlates very well with Cowley's calculations which include all possible three phonon combinations throughout the Brillouin zone. In view of the present discrepancy we plan further experimental work in other simple systems and suggest that additional theoretical calculations be made to reconcile theory and experiment.

ACKNOWLEDGMENTS

We would like to thank M. Reine for several useful discussions during the course of this work, and A. S. Pine for comments on an early draft of the manuscript, and R. A. Cowley for clarifying an aspect of his paper.

PHYSICAL REVIEW B VOLUME 1, NUMBER 2 15 JANUARY 1970

Role of Four-Phonon Processes in the Lattice Thermal Conductivity of Silicon from 300 to 1300°K*

Y. P. Joshi and M. D. Tiwari
Department of Physics, Allahabad University, Allahabad, India
and
G. S. Verma
Department of Physics, Banaras Hindu University, Varanasi, India

(Received 14 May 1969; revised manuscript received 30 July 1969)

It is shown that the high-temperature behavior of the lattice thermal conductivity of silicon, which has been carefully remeasured recently by Fulkerson *et al.*, can be explained by the four-phonon processes. It has been also found that the major contribution to the phonon thermal conductivity at high temperatures comes from the high-frequency transverse phonons.

INTRODUCTION

MEASUREMENTS of the thermal conductivity of silicon have been performed by a number of authors.[1–8] Maycock[9] has given an account of the recent work in this field. At elevated temperatures, the contributions of electrons and photons to the total thermal conductivity are appreciable, so that the lattice thermal conductivity is obtained from the total by substracting the former two contributions.[7,8] A comparison of the theory of lattice thermal conductivity to the experimental results is possible only if the calculation of the electronic contribution[10] based on the simple parabolic band, and the calculation of the radiation contribution,[11] are considered to be valid. For silicon and germanium, Holland[12] has shown that good agreement between experimental and theoretical results can be obtained at all temperatures if one considers the separate contributions of the longitudinal and transverse phonons. His formulation has also been applied quite successfully by Bhandari and Verma[13] to explain the high-temperature thermal conductivity of Si-Ge alloys. Recently, Fulkerson *et al.*[8] have shown that their thermal conductivity data for Si in the temperature range 100–1300°K cannot be explained by Holland's model of two-mode conduction. This discrepancy becomes more obvious when one considers the plot of thermal resistivity versus temperature T. For such a plot, the lattice thermal resistivity W is slightly different from a straight line, with an upward curvature, whereas Holland's analysis gives a downward curvature. This implies that the calculated thermal conductivity does not fall with temperature as rapidly as the experimental data. In other words, this suggests that there should be some extra phonon scattering process included which increases with temperature sufficiently rapidly and is responsible for the above result. The possible processes that can take place in a real crystal include the electron-phonon interactions[8] and the four-phonon processes.[7,14] It is also possible that the optical

---

* Work supported by the Council of Scientific and Industrial Research, India.

[1] B. Abeles, G. D. Cody, and D. S. Beers, J. Appl. Phys. **31**, 1585 (1960).

[2] A. D. Stuckes, Phil. Mag. **5**, 84 (1960).

[3] R. D. Morris and J. G. Hust, Phys. Rev. **124**, 1426 (1961).

[4] B. Abeles, D. S. Beers, G. D. Cody, and J. P. Dismukes, Phys. Rev. **125**, 44 (1962).

[5] R. G. Morris and J. L. Martin, J. Appl. Phys. **34**, 2388 (1963).

[6] H. R. Shanks, P. D. Maycock, P. H. Sidles, and G. C. Danielson, Phys. Rev. **130**, 1743 (1963).

[7] C. J. Glassbrenner and Glen A. Slack, Phys. Rev. **134**, A1058 (1964).

[8] W. Fulkerson, J. P. Moore, R. K. Williams, R. S. Graves, and D. L. McElroy, Phys. Rev. **167**, 765 (1968).

[9] P. D. Maycock, Solid State Electron. **10**, 161 (1967).

[10] J. K. Drabble and H. J. Goldsmid, *Thermal Conductivity in Semi-conductors* (Pergamon Press Inc., New York, 1961), p. 117.

[11] L. Genzel, Z. Physik **135**, 177 (1953).

[12] M. G. Holland, Phys. Rev. **132**, 2461 (1963).

[13] C. M. Bhandari and G. S. Verma, Phys. Rev. **138**, A288 (1965).

[14] E. F. Steigmeier and I. Kudman, Phys. Rev. **141**, 767 (1966).