Raman Scattering by Silicon and Germanium*

J. H. PARKER, JR., D. W. FELDMAN, AND M. ASHKIN
Westinghouse Research Laboratories, Pittsburgh, Pennsylvania

(Received 30 September 1966; revised manuscript received 2 December 1966)

Raman scattering from single-crystal Si and Ge at 300°K was measured using an argon laser as the exciting source. The first-order Raman spectrum yields energies for the $k\approx0$ optical modes of 520.2 ± 0.5 cm^{-1} for Si and 300.7 ± 0.5 cm^{-1} for Ge. These values are in reasonable agreement with other determinations. The full widths at half-intensity were found to be 4.6 cm^{-1} for Si and 5.3 cm^{-1} for Ge. These values are compared with theoretical predictions. A Raman band was observed in Si at 950 cm^{-1} which is attributed to second-order scattering and is compared with theoretical predictions.

INTRODUCTION

THE optical vibrational modes of lattices of the diamond structure are Raman[1] active but not infrared active in first order. Using visible exciting light one observes a single Raman line from the optic modes at $k\approx0$, where k is the wave vector of the mode. In a highly perfect intrinsic semiconductor crystal, the Raman line is broadened primarily by anharmonic forces, and a study of the line shapes gives information about these forces.

Measurements of the Raman-line position in Si have previously been reported by Russell.[2] The optical-mode frequencies at $k\approx0$ have also been obtained in Si and Ge directly from neutron scattering[3] and indirectly from a critical-point analysis of two-phonon infrared measurements.[4] Theoretical studies of the Raman spectra of Si and Ge have been made by Cowley[5] and and Klemens.[6]

Because of the indirectness of the infrared measurements and the low resolution of neutron-scattering experiments, Raman spectroscopy is the only technique presently available for determining optical-phonon lifetimes and precise values for the phonon frequency at $k\approx0$ for Si and Ge.

Because of the small interaction volume available, Raman spectroscopy with conventional light sources is extremely difficult in opaque materials, such as Ge and Si. However, the advent of lasers, and in particular the argon-ion laser, as monochromatic, high-intensity sources has made it possible to make high-resolution Raman-scattering measurements even in such materials.

We have measured the Raman frequency shifts and line shapes at room temperature. These data, which give the frequencies and linewidths of the optical vibrational modes at $k\approx0$ in single-crystal Si and Ge, are compared with the predictions of Cowley and Klemens. The relative first-order Raman intensity for these two materials and the second-order Raman scattering for Si have also been measured.

EXPERIMENTAL

Figure 1(a) shows a schematic diagram of the experimental arrangement used in the present study. The samples, acting as an additional mirror, were placed within the optical cavity (hemispherical) of the argon-ion laser.[7] The internal prism was used to select the operating wavelength of the laser. The laser was operated in the 4880 Å line for the majority of the measurements, and the Stokes component was normally observed. The Raman nature of the observed lines was confirmed in all cases; this was done by observing, in addition, either the anti-Stokes component for the 4880 Å line or the Stokes component for the 5145 or the 4765 Å line. The power incident onto the sample for the 4880 Å operation was of the order of 2 W. Figure 1(b) shows an expanded diagram of the sample orientation with respect to the incident beam and with respect to the direction of observation. An angle of incidence of approximately 82° was found empirically to yield the maximum Raman intensity. The incident

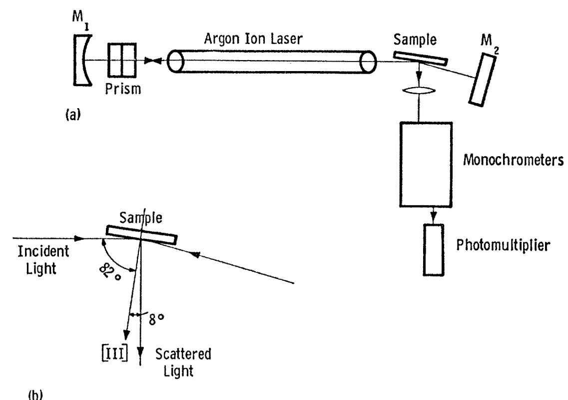

FIG. 1. (a) Experimental arrangement. (b) Detail of sample orientation.

* This work was supported in part by the U. S. Air Force Office of Scientific Research under Contract No. AF 49(638)-1589.

[1] R. Loudon, Advan. Phys. **13**, 423 (1964).

[2] John P. Russell, Appl. Phys. Letters **6**, 223 (1965).

[3] B. N. Brockhouse and P. K. Iyengar, Phys. Rev. **111**, 747 (1958); G. Dolling, in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1963), Vol. II, p. 37.

[4] F. A. Johnson and R. Loudon, Proc. Roy. Soc. (London) **A281**, 274 (1964).

[5] R. A. Cowley, J. Phys. (Paris) **26**, 659 (1965) and unpublished calculations; G. Dolling and R. A. Cowley, Proc. Phys. Soc. (London) **88**, 463 (1966).

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

[7] E. I. Gordon, E. F. Labuda, and R. C. Mallec, IEEE J. Quantum Electronics **QE-1**, 6 (1965).

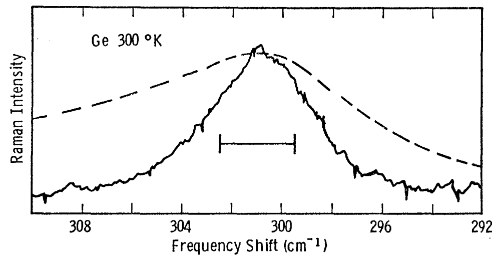

FIG. 2. First-order Raman scattering from Ge at 300°K. The dashed curve represents Cowley's theoretical calculations. The instrumental resolution is indicated by the vertical lines.

light was always polarized parallel to the surface of the sample. The scattered light was dispersed by two $\frac{1}{2}$-m grating monochromators operated in tandem so as to reduce the effect of Rayleigh scattering from the sample. The signal was detected with a cooled S-11 photomultiplier. The laser beam was chopped within the cavity at a rate of 540 Hz, and the signal from the photomultiplier was amplified and phase detected. The wavelength of the Raman lines was determined by using nearby calibrating lines of neon and argon. The samples were in the form of as-grown web strips[8] and electrolytically and mechanically polished disks from Czochralski-grown ingots, all of these being grown from nominally pure material. A boron-doped Si sample was used to gauge the effect of impurities on line position and width.

RESULTS

Figures 2 and 3 are typical experimental first-order Raman lines observed in Ge and Si, respectively. On each of the figures the instrumental resolution is shown. In each figure a theoretical curve (dashed) due to Cowley[9] is drawn. The experimental positions of the first-order lines differed from the peak positions of the theoretical curves by about 2%. In Figs. 2 and 3, the theoretical curves have been shifted by this amount to make the peak positions coincide. This difference may be attributed in part to the experimental uncertainty of the neutron measurements[3] on which Cowley's theory[5] is based, and possibly in part to an overestimation by Cowley of the anharmonicity. The experimental line position and linewidth were found to be the same for mechanically polished, electrolytically polished, and as-grown surfaces (web) when the starting material was nominally pure. For a Si sample containing boron at 5×10^{19} cm^{-3}, the width was found to be larger by about a factor of 2, and the position was shifted by not more

TABLE I. Frequency of the optical mode at $k\approx0$ (cm^{-1}).

	Present experiment	Russell[a]	Neutron[b]	Infrared[c]
Si	520.2 ± 0.5	522 ± 1	518 ± 8	522 ± 2
Ge	300.7 ± 0.5	...	300 ± 10	298 ± 2

[a] Reference 2.
[b] Reference 3.
[c] Reference 4.

than 1 cm^{-1}. Since this impurity level is at least three orders of magnitude higher than the nominally pure material, we conclude that the results obtained with the pure samples were not significantly affected by impurities.

Table I compares the present measured values of the optical-phonon frequencies with previous results. The present results are within the experimental accuracy of the infrared and neutron data, but disagree somewhat with Russell's Raman data on Si.

In Table II are listed the full widths at half-intensity

TABLE II. Measured and theoretical full widths at half-intensity for Ge and Si at 300°K (cm^{-1}).

	Experimental value	Klemens[a]	Cowley[b]
Si	4.6	8.2	14
Ge	5.3	4.4	17

[a] References 6 and 10.
[b] Reference 5.

which we obtain after correcting the measured line for the instrumental resolution. Also given, for comparison, are theoretical values of these quantities as calculated by Cowley[5] and as calculated by us using Klemens's theory.[10] An optical-mode lifetime is given by

$$\tau=2/Wc, \tag{1}$$

where τ is the lifetime in seconds, W the Raman linewidth given in Table II, and c the velocity of light. For silicon, τ is 1.5×10^{-11} sec and for germanium τ is

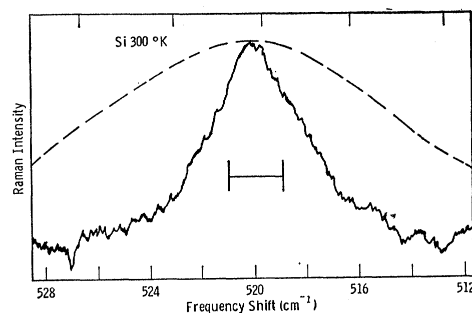

FIG. 3. First-order Raman scattering from Si at 300°K. The dashed curve represents Cowley's theoretical calculation. The instrumental resolution is indicated by the vertical lines.

[8] S. O'Hara and A. I. Bennett, J. Appl. Phys. 35, 686 (1964).

[9] The dashed curve of Fig. 2 is curve A of Fig. 6 in Ref. 5. The dashed curve of Fig. 3 is the corresponding curve for Si (derived from unpublished calculations due to Cowley). These theoretical curves do not include terms corresponding to higher-order phonon processes as discussed by Cowley. The inclusion of such contributions probably would not affect the lack of agreement between Cowley's theory and our experimental results.

[10] The value for Si was recalculated, with slightly modified parameters, from those originally used by Klemens.

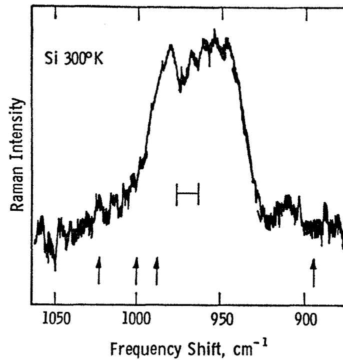

FIG. 4. Second-order Raman scattering from Si at 300°K. The arrows indicate the positions of prominent peaks in Cowley's theoretical calculation. The instrumental resolution is indicated by the vertical lines.

1.3×10^{-11} sec. Equation (1) is strictly valid only if the line shape is Lorenzian. The experimental signal-to-noise ratio was not sufficiently high to allow us to decide if the line shape was Lorenzian and therefore the applicability of Eq. (1) is somewhat questionable.

Even with the reservation that the line shape of Cowley's theory is quite asymmetric and therefore the comparison of a theoretical half-width with an experimentally determined one may be somewhat misleading, his theory appears to overestimate the effects of anharmonicity on lifetime. Furthermore, the measurements are accurate enough to show the predicted asymmetry of the line if present, but from Figs. 2 and 3 the lines are seen to be almost symmetrical. In comparing Klemens's theory with experiment, only order-of-magnitude agreement should be expected, which is found to be the case. It should be noted that additional linewidth due to the breakdown in the momentum selection rule associated with the finite penetration depth of the exciting light at the surface is negligible.

Figure 4 shows a broad reproducible Raman band observed for Si. We suggest that this band is the second-order Raman spectra for Si. The vertical arrows in Fig. 4 indicate the locations of the large peaks of the different second-order terms calculated by Cowley. The relative strengths of some of these terms are not given by the theory, and thus the theory does not give the shape of the Raman emission spectrum. The difference in frequency between the observed Raman band and the region of the arrows is within the uncertainty of the phonon frequencies used to determine the theoretical spectra. The ratio of the peak intensity of the second-order band to the peak of the first-order line was found experimentally to be approximately 3×10^{-3}.

The measurements of the relative intensities of first-order Raman-scattered light for Ge and Si can be used in the following way to compare the values of the changes in the electronic polarizability with lattice distortion in these two materials. The Born and Huang[11] description of the Raman effect in terms of an effective electronic polarizability operator **P** will be used. This polarizability is expanded in the relative displacement of the two sublattices, and the coefficients of the linear terms are denoted by a. When account is taken of the incoherent power loss due to absorption in reaching a scattering element and then returning to the surface of the crystal, the ratio of the scattered intensities can be written

$$I_{\mathrm{Si}}/I_{\mathrm{Ge}}=[\alpha M\omega/a^2(n(\omega)+1)]_{\mathrm{Ge}}\times[a^2(n(\omega)+1)/\alpha M\omega]_{\mathrm{Si}}, \quad (2)$$

where the subscript on the square bracket denotes that the quantities it encloses are for the material noted; M and ω are, respectively, the ionic mass and frequency of the optical mode; $n(\omega)$ is given by $[\exp(\hbar\omega/kT)-1]^{-1}$, with T the temperature; and α is the linear absorption coefficient at the laser frequency and at 300°K. The absorption coefficients are[12,13] $\alpha_{\mathrm{Ge}}=5.5\times10^5$ cm^{-1} and $\alpha_{\mathrm{Si}}=2\times10^4$ cm^{-1}. At room temperature, Eq. (2) gives

$$I_{\mathrm{Si}}/I_{\mathrm{Ge}}\approx 33a^2_{\mathrm{Si}}/a^2_{\mathrm{Ge}}.$$

The measured value of the intensity ratio is $I_{\mathrm{Si}}/I_{\mathrm{Ge}}\sim 10$ to 20 and therefore $a_{\mathrm{Si}}/a_{\mathrm{Ge}}\sim 0.5$ to 0.8.

ACKNOWLEDGMENTS

The authors wish to thank P. G. Klemens for helpful discussions, J. W. Faust, Jr., and M. W. Larkin for Si and Ge samples, E. I. Gordon for the argon-laser design and Miss B. J. Kagle for assistance in numerical analysis.

[11] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, England, 1954), Chap. IV.
[12] H. R. Philipp and E. A. Taft, Phys. Rev. **113**, 1002 (1959).
[13] W. C. Dash and R. Newman, Phys. Rev. **99**, 1151 (1955).