First-order Raman spectrum of diamond at high temperatures

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Measurements of the first-order Raman spectrum in natural type-IIa diamond for the temperature range of 293 to 1850 K are presented. Both the Stokes and anti-Stokes components are analyzed for their intensity, Raman shift, and width variation with temperature. Optical pyrometry was used to make the temperature measurements, the results of which were independently confirmed by the Stokes–to–anti-Stokes intensity ratios. The shift and width variations with temperature are in general agreement with the molecular-dynamics simulations of C. Z. Wang, C. T. Chan, and K. M. Ho [Phys. Rev. B **42**, 11 276 (1990)]. Heating of the samples to temperatures as high as 1850 K *in vacuo* could be performed without any evidence of polymorphic conversion to graphite, also in agreement with previous investigations. Our experimental first-order Raman shifts, using units of cm^{-1} and absolute temperature, are conveniently expressed as $\Delta v = a_1 T^2 + a_2 T + a_3$ with the coefficients found to be -1.075×10^{-5} $cm^{-1} K^{-2}$, $-0.007\,77$ $cm^{-1} K^{-1}$, and 1334.5 cm^{-1}, respectively.

I. INTRODUCTION

The room-temperature Raman spectrum of natural diamond was measured by Robertson and Fox,[1] and Ramaswamy[2] in 1930, within two years of the discovery of the Raman effect.[3] It is well known that the lattice dynamics that give rise to the Raman effect also determine the thermal properties such as the specific heat and thermal conductivity.[4] There has been a great deal of interest in the thermal properties of diamond, as diamond is superior in this respect to most materials and chemically inert in air at temperatures below approximately 700 K.[5] The recent success in synthesizing diamond films from the vapor phase[6-8] has opened up a wide range of applications that include the integration of diamond into high-power microelectronics[9] and the use of diamond in infrared optics.[10] Understanding phonon behavior related to the anharmonic effects in the bonding between carbon atoms in diamond at high temperatures is of fundamental importance to the understanding of the high-temperature properties of diamond and diamond films.

Despite the great interest in diamond and particularly in diamond films as an industrial material, there are no theories based on first principles that can accurately predict the thermal properties of diamond over a wide range of conditions. This is in part due to the limited knowledge that we have of the shape of the interatomic potential between carbon atoms in the diamond lattice. Semiempirical model potentials have been employed in the past in molecular mechanics simulations, and have been used to predict the bulk behavior of diamond at room temperatures.[11-13] An extension of this approach to higher temperatures is desirable. Furthermore, the ability to accurately predict the behavior of the first- and second-order Raman spectrum of diamond with temperature would be a true test of the anharmonic contributions to the employed potential.

Recently, Wang, Chan, and Ho[14] used an empirically derived tight-binding potential[15] in a molecular-dynamics simulation to compute the temperature dependence of the first-order Raman spectrum of diamond and silicon. As expected, they observed considerable shifting to lower energy and broadening of the first-order Raman spectra with temperature. This was illustrated in a generalized theory by Viswanathan,[16] who attributed the decrease in the Raman shift and increase in the broadening of the Raman line to the mechanical anharmonicity. Wang, Chan, and Ho obtained very good agreement between their computed spectra and the experimental data available for silicon. No comparison was made of their computed spectra with experimentally determined ones of diamond, although such a comparison would be very informative, and would demonstrate the usefulness of their tight-binding potential in computing the high-temperature variation of diamond's thermal and mechanical properties.

The temperature variation of the first-order Raman spectrum in diamond was first investigated by Nayar in 1941 (Ref. 5) and further discussed by Raman,[17] in an attempt to understand its relationship to the thermal expansion of diamond, as well as to the polymorphic transition of diamond to graphite. The transition temperature *in vacuo* has been predicted[18] and observed[19,20] by many investigators to be approximately 2100 K. Shortly following the measurements of Nayar which ranged in temperature from 85 to 1130 K, Krishnan[21] performed more extensive experiments, over a similar range of temperatures. Both Nayar and Krishnan used the measured variation of the Raman shift Δv with temperature T, i.e., $d\Delta v / dT$, in conjunction with the compressibility and specific heat to infer the thermal expansion coefficient. In both cases, the highest temperatures achieved were limited by diamond contamination and thermal emission, the latter contributing as background interference. With the exception of the study by Solin and Ramdas[22] of the first-

and second-order Raman spectrum of diamond at temperatures between 15 and 300 K, there has been little work on the subject since Krishnan's study in 1946. In this paper, we report what we believe is the first detailed study of the temperature dependence of the first-order Raman spectrum in natural diamond at temperatures above 1000 K.

II. EXPERIMENT

Raman spectra were obtained by exciting natural diamond with the 457.94-nm output from an argon-ion laser (Lexel Model 85) mechanically chopped at 2 kHz. A schematic of the facility is given in Fig. 1. The incident laser direction was along the [100] or x axis, i.e., normal to the polished (100) face of a natural type-IIa diamond sample with dimensions 2 mm×2 mm×250 μm. The laser was linearly polarized along the [010] or y axis of the sample. The forward scattered light, unanalyzed for its polarization, was detected through the diamond sample with $f/4$ collection optics. All polarization components of the scattered light were intentionally collected as it was found that the anti-Stokes component at high temperatures was significantly depolarized. A 1-m scanning monochromator (Jarrel-Ash Model 75-154) was used in conjunction with appropriate bandpass filters to discriminate the Raman components against background and Rayleigh interferences. The monochromator entrance and exit slit widths were both 100 μm, giving rise to approximately 0.1-nm spectral resolution. A Hamamatsu Model 2801 photomultiplier was used at the exit slit of the monochromator. The resulting signal was amplified by two stages of a low noise Stanford Research Systems Model 440 amplifier. A Stanford Research Systems Model 400 photon counter, set to discriminate against low-energy dark-noise pulses, accumulated the counts. A tungsten filament lamp was used to determine the relative system response. All intensities are measured in power units rather than photon count rates.
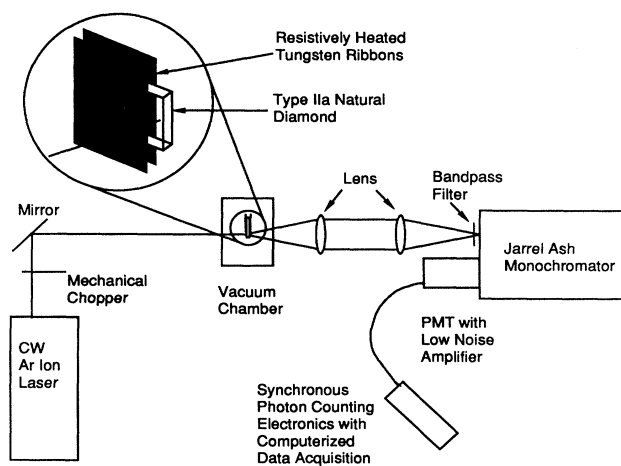

FIG. 1. Schematic of experimental setup for forward Raman scattering studies of natural diamond at high temperature. The enlargement illustrates the mechanism employed to heat, hold, and interrogate the sample.

Background signal subtraction was essential in order to discriminate between the inelastically scattered light and intrinsic thermal radiation from the diamond sample at the high temperatures. We employed a dual channel detection scheme, with one channel gated such that it detected scattered light coincident with the chopped laser pulse, and the second channel gated to detect background light while the laser was blocked by the mechanical chopper. The experimental approach taken here was similar to that of Nemanich et al.,[23] who studied the Raman spectrum of silicon near the melting point.

The diamond sample was sandwiched between two electrically heated tungsten ribbons and was free to thermally expand, as shown in the inset to Fig. 1. With this geometry, the diamond was nearly completely surrounded by the tungsten filaments, and would come to thermal equilibrium with the filament through radiant energy exchange. The tungsten temperature was measured by optical pyrometry, with a Pyro Micro Model 85 disappearing filament pyrometer, making appropriate correction for the tungsten emissivity.[24] In order to verify that the diamond was in thermal equilibrium with the tungsten filaments, its temperature was independently determined from the Stokes–to–anti-Stokes component intensity ratios, as discussed in Sec. III. The diamond sample and filament heaters were placed within a specially designed high vacuum chamber with optical access. The chamber pressure during runs was maintained below 10^{-5} torr, thereby preventing contamination due to oxidation or premature graphitization of the diamond sample. Potential contamination was assessed by monitoring the transmission of nearby argon-ion plasma emission lines originating from the laser discharge tube. These lines also served as accurate and absolute wavelength references. When measuring the Raman scattering components using 457.94-nm laser line excitation, the nearby Ar^+ $4s\,^2P \rightarrow 4p\,^2D°$ line at 487.986 nm lay reasonably close to the Stokes component, and the $4s''\,^2S \rightarrow 5p\,^2P°$ and $3d\,^2F \rightarrow 4p'\,^2D°$ unresolved spectral lines at 430.924 and 430.909 nm were sufficiently close to the anti-Stokes component. These emission lines also served as convenient references for the instrument contribution to the Raman line broadening, as they were predominantly instrument broadened under conditions expected within the laser discharge cavity.

III. RESULTS AND DISCUSSION

Typical Stokes and anti-Stokes first-order Raman spectra of diamond at a temperature of 1470±40 K are shown in Fig. 2. The nearby argon plasma emission lines appear at 1345 and 1370 cm^{-1} shifts. As expected, the observed Stokes and anti-Stokes shifts are equal and approximately 1300 cm^{-1}, and considerably less than the room-temperature shift of 1332.5 cm^{-1} for diamond.[22] In addition, the lines are significantly broader than the nearby argon plasma reference lines.

The variation in both the Stokes and anti-Stokes component intensities with temperature for a particular experimental run is shown in Fig. 3. These data are in very good agreement with quantum-mechanical predictions[25] for the intensities' temperature variation, given here as
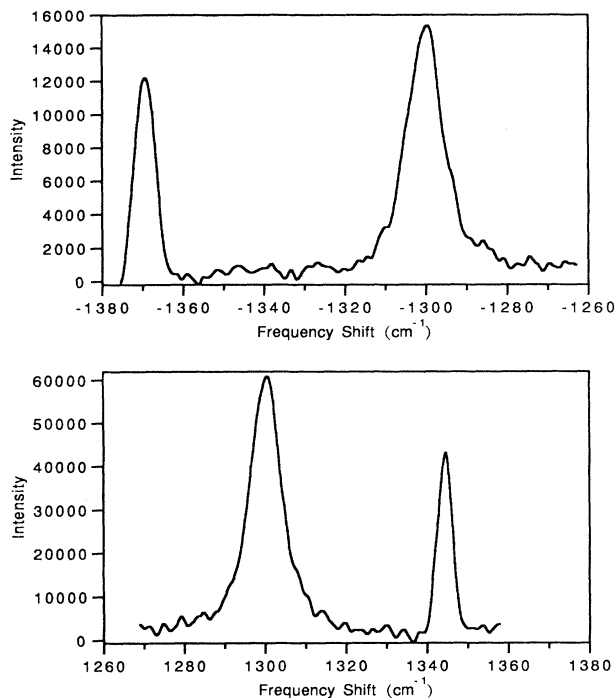
FIG. 2. Anti-Stokes, top, and Stokes Raman spectra with argon-ion emission calibration lines. The diamond temperature was 1470 K.

$$I_{St} \propto \frac{\hbar}{2\omega_s}(\omega_l - \omega_s)^4 [1 + (e^{\hbar\omega_s/kT} - 1)^{-1}] , \qquad (1)$$

$$I_{a\text{-}St} \propto \frac{\hbar}{2\omega_s}(\omega_l + \omega_s)^4 (e^{\hbar\omega_s/kT} - 1)^{-1} . \qquad (2)$$

Here ω_s is the phonon frequency, ω_l is the line center frequency of the laser excitation source, T is the sample

temperature measured by optical pyrometry, and h and k are the Planck and Boltzmann constants. The proportionality constant in Eqs. (1) and (2) include the variation in the polarization with normal coordinate separation and the collection efficiency of the optics, and are essentially equal for both the Stokes and anti-Stokes components. The close agreement between the measured and theoretical temperature dependence suggests that the sample is optically thin to the laser, Stokes, and anti-Stokes radiation. This is as expected for diamond, and no corrections have been made for self-absorption.

The Stokes–to–anti-Stokes intensity ratio

$$\frac{I_{St}}{I_{a\text{-}St}} = \left[\frac{\omega_l - \omega_s}{\omega_l + \omega_s} \right]^4 e^{\hbar\omega_s/kT} \qquad (3)$$

can be a direct measure of the sample temperature. Indeed, this has been used as an unambiguous measure of sample temperature in a range of materials by many investigators.[23,26,27] For the excitation source used in the present experiments, the variation of this ratio with temperature is shown in Fig. 4 (solid curve), along with the experimentally derived data of a number of experimental runs. The good agreement between theory and experiment once again indicates that self-absorption was not significant here, and that the diamond sample temperature was not appreciably different from that of the tungsten heaters.

Variation in the observed Raman shift with temperature for both the Stokes and anti-Stokes components is shown in Fig. 5. Also shown in the figure is the earlier data of Nayar[5] and Krishnan.[21] Our data represent a major extension of the earlier work, and suggest that the lower-temperature range measurements of this study are in better agreement with the results of Krishnan than those of Nayar, although neither of the earlier studies reported any confidence levels or accuracy in the measured shifts and temperatures. Our uncertainties in frequency shift are ± 0.3 cm^{-1} and are less than the size of the sym-
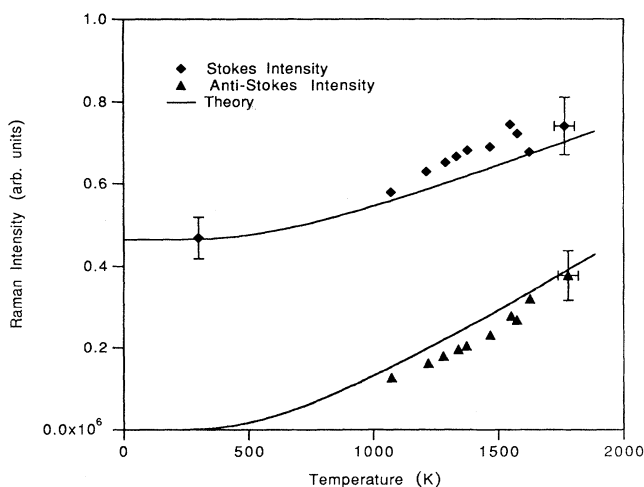

FIG. 3. Stokes and anti-Stokes Raman intensity variation with temperature for type-IIa natural diamond. The solid lines represent the temperature variation predicted by general quantum-mechanical theory.
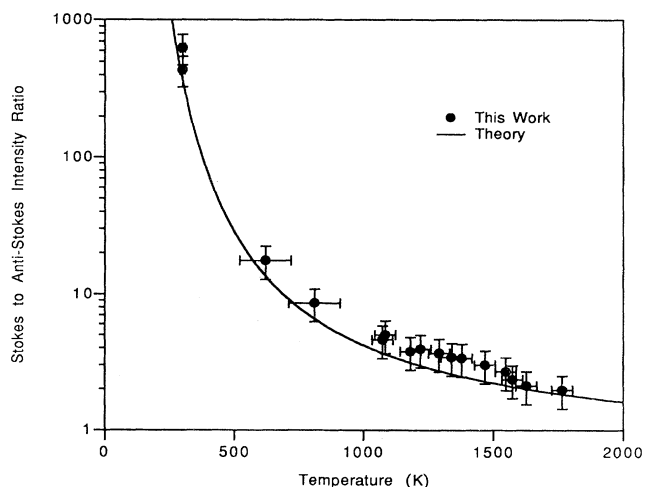

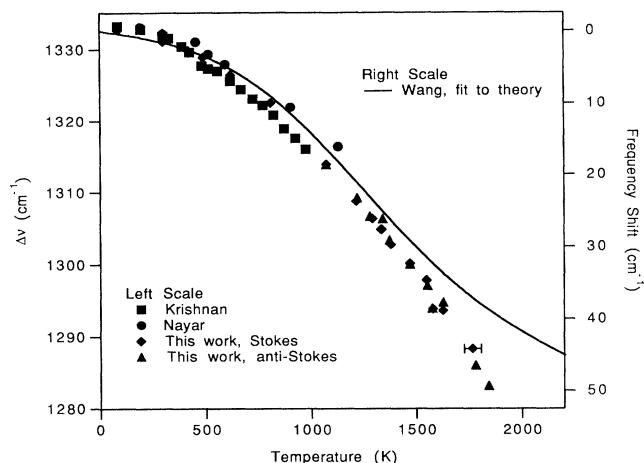FIG. 4. Comparison of measured and theoretical Stokes–to–anti-Stokes intensity ratios.

FIG. 5. Variation of the first-order Raman shift in diamond with temperature. The data shown are a compilation of previous work of Nayar (Ref. 5), Krishnan (Ref. 21), and of this work. The solid line represents a fit to the results of molecular-dynamics simulation of Wang, Chan, and Ho (Ref. 14).

bols used to represent the data points. The error in the temperature arises primarily from the uncertainties in the use of the disappearing filament pyrometer for measuring the tungsten temperature. The solid line in Fig. 5 represents a curve fit to the theoretical data presented by Wang, Chan, and Ho.[14] The theoretical predictions compare quite well with experimental shifts at temperatures below 1500 K, but are well outside the estimated range due to experimental error in the measured values above 1500 K. An extrapolation of our data to high temperatures would give significantly different results from the corresponding calculations of Wang, Chan, and Ho. We find that our data are well represented by the curve

$$\Delta v = a_1 T^2 + a_2 T + a_3$$

with the coefficients found to be -1.075×10^{-5} cm^{-1} K^{-2}, -0.00777 cm^{-1} K^{-1}, and 1334.5 cm^{-1}, respectively, with a standard deviation of 3.6×10^{-7}, 7×10^{-4}, and 0.3, respectively. This simple functional form is significantly different from that originally proposed by Viswanathan,[16] as it was found that that function failed to adequately describe the behavior at lower temperatures.

The variation in the full width at half maximum intensity (FWHM) with temperature is shown in Fig. 6. Also shown for comparison are the experimental data of Krishnan[21] and the theoretical predictions of Wang, Chan, and Ho.[14] The spectral line shapes were found to be well represented by a Voigt function. The Lorentzian Raman scattered contribution to the line shape was found by deconvolving the Gaussian instrument broadening from the actual spectra. The instrument broadening contribution to the measured spectra was Gaussian in shape, with a FWHM of 3.7 and 4.7 cm^{-1} for the Stokes and anti-Stokes lines, respectively. As can be seen from Fig. 6, our results are in excellent agreement with the previous measurements of Krishnan.[21] Furthermore, the experimental results are in overall agreement with the
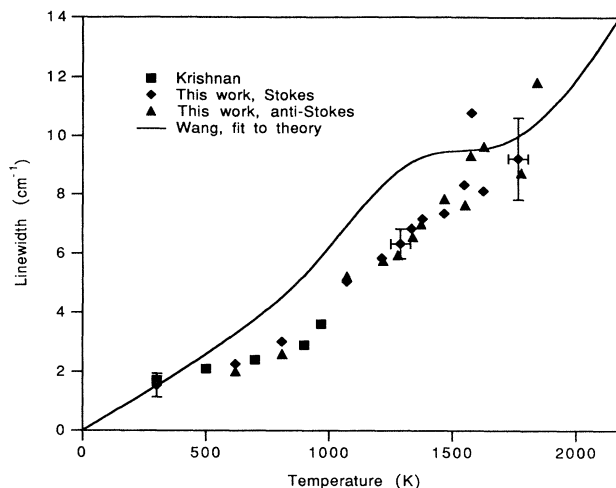

FIG. 6. Variation of the full width at half maximum of the first-order Raman spectrum in diamond with temperature. The data shown are a compilation of previous work of Krishnan (Ref. 21) and of this work. The solid line represents a fit to the results of molecular-dynamics simulation of Wang, Chan, and Ho (Ref. 14).

predictions of Wang, Chan, and Ho,[14] particularly at the lower temperatures (< 1000 K) and higher temperatures (> 1500 K) investigated here. There is some discrepancy between theory and our data at temperatures between 1000 and 1500 K.

No evidence of graphitization was observed at the highest temperatures studied (1850 K), consistent with other observations.[19,20] Our experiments described here were limited to temperatures below 1850 K, primarily a result of high levels of background thermal radiation. We are now modifying the facility to employ a high repetition rate diode pumped Nd:YLF (yttrium lithium fluoride) laser excitation[28] (2 kHz, 10 ns pulse duration), which would increase our signal to background interference ratio substantially and would allow us to explore the temperature range above 1850 K.

IV. SUMMARY

We have presented experimental results describing the temperature variation in the first-order Raman spectrum of diamond. The observed broadening and shifting of the Stokes and anti-Stokes components arising from thermal expansion and anharmonic coupling is in general agreement with recent theoretical predictions of Wang, Chan, and Ho.[14] Further investigation is now in progress, to explore the temperature range above 1850 K, where the measured shifts appear to be deviating substantially from those predicted.

ACKNOWLEDGMENTS

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