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Temperature dependence of the first-order Raman phonon line of diamond

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Micro-Raman scattering from single-crystal diamond was performed over the temperature range 77–873 K. These measurements show that the Raman phonon frequency and the linewidth are temperature dependent, the linewidth and the frequency extrapolated to 0 K are $1.103\pm0.03\,\mathrm{cm}^{-1}$ and $1332.7\pm0.2\,\mathrm{cm}^{-1}$, respectively. A linear relationship was found to exist between the downshift of the Raman frequency and the linewidth. In contrast to other group IV semiconductors, we show that in diamond the dependence of the phonon linewidth on the temperature is well described by the simple Klemens model which assumes that the zone center phonons decay into two acoustical phonons of opposite momentum but belonging to the same acoustic branch.

I. INTRODUCTION

Diamond is one of the wide band-gap materials. It has great potential in the future electronic and optoelectronic devices owing to its high-temperature stability, novel electronic, and superior mechanical properties.[1] Investigation of the temperature effect on the optical phonons of diamond provides insight into the atomic structures and bonding properties of diamond. The temperature dependence of the vibrational frequencies and linewidths of diamond have been widely studied in the past, both experimentally (Krishnan,[2] Solin and Ramdas,[3] Anastassakis, Hwang, and Perry,[4] Borer, Mitra, and Namjoshi,[5] Herchen and Cappelli,[6] Zouboulis and Grimsditch,[7] and Cui *et al.*[8]) and theoretically (Klemens,[9] Cowley,[10] and recently by Debernardi, Baroni, and Molinari[11]). The experimental results differ considerably between the different authors, in particular the full width at half maximum (FWHM) extrapolated to zero temperature has been reported to vary from 2.9 cm^{-1} (Ref. 2) to 1.48 cm^{-1}.[3] Theoretical calculations of the low-temperature FWHM also differ widely from 0.035 cm^{-1} (Ref. 9) to 2.74 cm^{-1} (Ref. 10) and very recently to 1.01 cm^{-1}.[11]

In general, the temperature effect interpreted in terms of anharmonic processes would lead to a better understanding of the electronic properties and application of semiconductors at different temperatures. For example, the Raman linewidth is a measure of the lifetime τ of the optical phonons, which is now in the time domain of fast pulsed lasers. Raman spectroscopy is very appropriate for the investigation of the effects of temperature, stress, doping, and defects, etc. on the optical phonons of diamond and diamondlike materials (see, e.g., Ref. 12 and references therein). The temperature dependence of FWHM has been carefully measured in diamond-type semiconductors such as Si,[13–15] Ge,[15] GaAs,[16] and GaN,[17] etc. These experimental data have been interpreted assuming second-order cubic anharmonic potentials,[15] or even higher-order terms.[13,14] In the most recent *ab initio* calculations, Debernardi, Baroni, and Molinari[11] considered up to third-order process and obtained good agreement with the experimental results of Menendez and Cardona[15] on Si and Ge. However, that work did not report any comparison between the Debernardi theory and the experimental results for diamond. Such a comparison is important because the calculations of Debernardi, Baroni, and Molinari[11] predict that unlike the case of Si or Ge, the dominant mode for zone-center phonon decay of diamond is predominantly via decay into two acoustical phonons from the same branch. Therefore a comparison between experiment and theory will help to elucidate the microscopic processes of phonon decay in diamond.

In the present paper careful measurements of the full width at half maximum and the Raman frequency shift of diamond have been carried out at different temperatures. The temperature effect on the phonon is interpreted in the framework of the generalized Debernardi model and the more restricted Klemens model which has been predicted to be very relevant for diamond, though it is clearly inadequate for other diamond-structure materials such as Si or Ge. We also explain the anharmonic nature of the linear relationship between the linewidth and the Raman shift.

II. ANHARMONIC EFFECT ON THE RAMAN PHONONS

The anharmonic effect on the first-order Raman phonon of diamond is to change its harmonic frequency at the center of the Brillouin zone to a damped frequency. In the standard anharmonic approximation, the zone-center phonon decays into two acoustical modes with opposite momentum whose frequencies sum up to the frequency of the LO-TO zone-center phonon, and the linewidth is a function of the third derivative of the energy with respect to the displacement vectors. The models which explain these anharmonic effects differ by assuming different decay channels. Klemens[9] assumed that the zone-center optical modes decay into two acoustical phonons of opposite momentum which belong to the same acoustical branch. On the other hand, Cowley[10] and Debernardi, Baroni, and Molinari[11] considered all the possible decay channels belonging to different branches, and Debernardi, Baroni, and Molinari developed a complete first-principle approach to the anharmonic decay of phonons. De-

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bernardi, Baroni, and Molinari[11] pointed out that for diamond, the Klemens approximation becomes the dominant zone-center decay mode at the expense of the LA+TA decay channels which were the dominant ones for the other materials displaying the diamond structure such as Si and Ge.[15] The Klemens approximation is a good one for diamond because the two phonon density of states at the zone center is high, which is not the case for Si or Ge, and thus the probability for decay into two acoustic phonons of opposite momentum is enhanced.

A detailed calculation of the anharmonic coupling between zone-center phonons and two acoustic modes with opposite momenta has been proposed by Cowley.[10] The work which applies to diamond is an extension of previous Green's-function calculations by Maradudin and Fein.[18] More recently, Balkanski, Wallis, and Haro[14] explained the temperature dependence of the Raman line shape of Si by including the decay of zone-center modes into more than two acoustical phonons with opposite momenta. Debernardi, Baroni, and Molinari[11] gave the *ab initio* calculation of the anharmonic phonon lifetimes in semiconductors, such as Si, Ge, and C, from density-functional perturbation theory.

In the anharmonic approximation, the zone-center unperturbed frequency ω_0 undergoes a complex shift $\Delta\omega(q,j)+i\Gamma(q,j)$, the real part redshifts the normal-mode frequency, and the imaginary part, which is the reciprocal of the phonon lifetime, is usually referred to as the linewidth. Both parts are temperature dependent. According to Cowley, the three lowest contributions in the self-energy which contribute to the anharmonic interaction arise (i) from the thermal expansion which shifts the zone-center mode but does not modify the Raman width. (ii) From the cubic anharmonic term which expands the Hamiltonian to the second order, this term modifies both the real and the imaginary part of the self-energy. (iii) From the quartic anharmonic term which changes the zone-center frequency but does not broaden the Raman line.

The contributions to the Raman shift arising from the first and from the third term have not been considered by Cowley and later authors, because these two terms have opposite signs and are almost equal to each other and hence tend to cancel out.[19] In the anharmonic approximation, the line shape of the Stokes peak is given by[15]

$$I_s(0,j,\Omega)\propto\frac{\Gamma(0,j,\Omega)}{[\omega(0,j)+\Delta(0,j,\Omega)-\Omega]^2+\Gamma^2(0,j,\Omega)}\times[n(\Omega)+1], \tag{1}$$

where Ω is the dressed frequency, $\omega(0,j)$ represents the harmonic Raman frequency at the zone center, the index j refers to the LO branch, and $n(\Omega)$ the thermal occupation number. At temperature T, the anharmonic interactions change the harmonic frequency into a damped frequency:

$$\omega(0,j|T)=\omega(0,j)+\Delta(0,j|T)+i\Gamma(0,j|T) \tag{2}$$

in place of $\omega(0,j)$ which is the unperturbed Raman frequency at 0 K.

When the zone-center phonon decays into two acoustic phonons with opposite momenta, which belong to different branches j_1 and j_2, the general expression for the linewidth is

$$\Gamma(T)=\Gamma_0\{1+n(q,j_1)+n(-q,j_2)\}, \tag{3}$$

where Γ_0 is the linewidth at zero temperature. In the more restrictive case of decay into acoustic phonons with opposite momenta but originating from the same branch, namely the Klemens channel,[9] the temperature dependence of the linewidth is simplified into

$$\Gamma(T)=\Gamma_0\left(1+\frac{2}{e^{\hbar\omega_0/2k_BT}-1}\right), \tag{4}$$

where ω_0 is the zone-center phonon energy at zero K, k_B is the Boltzmann factor, and T the absolute temperature.

In the second term of the Cowley expansion, the real and the imaginary part of the self-energy are Kramers-Kronig related. The Raman line shift away from the unperturbed Raman frequency, which the is real part of the self-energy, should follow the same temperature dependence as $\Gamma(T)$ with an opposite sign, i.e.,

$$\Delta\omega(T)=-A\left(\frac{2}{e^{\hbar\omega_0/2k_BT}-1}\right), \tag{5}$$

where the constant ''A'' depends on the details of the diamond dispersion curves.

III. EXPERIMENTAL DETAILS

The diamonds used in this experiment are natural type-IIa diamond slabs with dimensions of $3\times3\times0.25\,\mathrm{mm}^3$ and polished to provide a (001) facet surface. In this set of experiments, great care was given to obtain maximum possible accuracy. The triple *X-Y* Dilor spectrometer was used in the ''additive mode'' where the three holographic gratings were in series. Each pixel of the cooled charge-coupled device detector corresponds to a spacing of 0.2 cm^{-1}. As each peak is described by many pixels, the accuracy in the determination of the peak position and FWHM which take into consideration the entire spectrum was found to be 0.02 cm^{-1}. Diamond is transparent to the 514.5-nm line of the Ar^+ ion-laser line. We used a X50 microscope objective, and a confocal pinhole which reduced the analyzed volume to a cylinder about 2.5 μm in diameter and 5-μm depth. The Raman frequency was calibrated with reference to the first-order Si phonon frequency. The Raman spectra were taken in the $z(yx)\overline{z}$ backscattering configuration. In order to avoid sample heating, the incident laser power on the sample was less than 2 mW.

A Linkam temperature stage with a quartz window was used to vary the sample temperature from 78 to 873 K in flowing nitrogen. In order to eliminate possible oxidation effects, the pressure of flowing nitrogen was maintained slightly exceeding one atmosphere. The temperature stability was estimated to be ±5 K at high temperature. For each measurement point, the temperature was stabilized for 10 min before acquiring a spectrum for 2 min. At each given temperature, two Stokes component spectra were measured and averaged to obtain the experimental spectrum. To ensure a signal-to-noise ratio greater than 100:1, small slits and long integration times were used. The presence of the quartz window of the heating stage caused some increase in the background noise level which was taken into account in the data processing of the Raman spectra. The measurements were repeated for a few samples to ensure reproducibility. Taking into account variations between samples and the intrinsic instrument error, the overall wave-number error was estimated to be in the range of $\pm 0.2\ \mathrm{cm}^{-1}$ at any given temperature.

Natural diamond normally displays a zone-center Raman line at $1332.2\ \mathrm{cm}^{-1}$ at room temperature. This Raman intensity varies with polarization and scattering geometry. For backscattering $z(yx)\overline{z}$ geometry we used in experiments, the incident laser was polarized parallel and the detected Raman perpendicular to the [001] axis of the diamond crystal. In this orientation Raman-scattering intensity is maximized.

IV. RESULTS AND DISCUSSION

The diamond Raman spectra are found strongly affected by temperature changes. With increasing temperature, the Raman peak is shifted toward lower frequency, and the full width at half maximum increases.

The observed Raman peak is the convolution of the Lorentzian shape of the actual phonons with the response function of the instrument. This function, which originates mainly from the effect of different slit widths on laser beam, should have an approximate Airy disc shape or Gaussian shape. However, the Gaussian and Airy functions are almost identical (to within 3%, see Ref. 15) and commonly the response function is considered to be of a Gaussian type. For the spectral fit of measured Raman lines, we used modified Lorentzian line shape (the so-called Voigt profile which is a mixture of Gaussian and Lorenztian line shapes). The Gaussian component contribution to the linewidth was deconvoluted, leaving a pure Lorentzian form. In this way, the FWHM data in this paper have been corrected for the instrument response function.

A. Linewidth dependence on temperature of the first-order Raman phonon

In Fig. 1, the open circles show the dependence of the Raman line broadening parameter $\Gamma(T)$ as a function of temperature. At high temperature, the linewidth increases approximately linearly, at low temperature it converges to about $1.1\ \mathrm{cm}^{-1}$ at zero temperature. On the same figure, we also give the results of Borer, Mitra, and Namjoshi[5] (squares) and Herchen and Cappelli[6] (solid diamonds). Their linewidth $\Gamma(T)$ have a similar temperature dependence behavior, but our experimental results give a smaller linewidth extrapolated to zero temperature.

The calculation of the FWHM depends on the details of the complete phonon dispersion curves, and one of the most complete *ab initio* calculations has been carried out by Debernardi, Baroni, and Molinari,[11] in which the eigenfrequencies and the eigenvectors were deduced from the lattice-dynamical calculations in the harmonic approximation. In this reference and in Ref. 15 the relative contribution of the individual decay channels were calculated which show that the Klemens decay channels should be a good approximation to describe the FWHM dependence on temperature in diamond. From Fig. 1, we see a good description of the temperature behavior of the linewidth of diamond using the Klemens model. Using Eq. (4) and the extrapolated value of the Raman frequency at 0 K, $\omega(T=0\ \mathrm{K})=1332.7\ \mathrm{cm}^{-1}$, the linewidth at $T=0$ K was found to be $\Gamma(T=0)=1.103 \pm 0.03\ \mathrm{cm}^{-1}$.

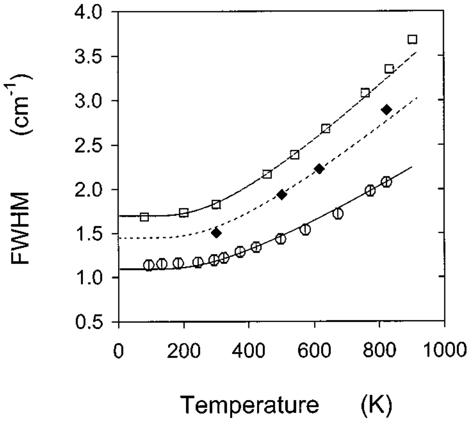

FIG. 1. Temperature dependence of linewidth Γ for the first-order Raman mode in diamond (open circles). The solid diamonds and open squares are from Herchen and Cappelli (Ref. 6) and Borer, Mitra, and Namjoshi (Ref. 5), respectively. The solid curve and dashed curves give the theoretical fit to the measurements according to Klemens decay channel, Eq. (4).

Table I summarizes to date the main experimental and theoretical results of FWHM at zero temperature. Reference 3 obtained $1.48\ \mathrm{cm}^{-1}$ with an instrumental resolution of 0.4 cm^{-1}. Reference 5 quoted $1.68\ \mathrm{cm}^{-1}$ and comments that this value had been corrected to ''zero'' slit width. Reference 7 did not measure below the room temperature but extrapolates to zero temperature based on a fit of the experimental values using Klemens' model. We note the discrepancy between our FWHM values and the results reported in Refs. 3, 5, 6 and 7. We suspect that the main reason for this is that our results were carefully corrected for the response of the instrument as explained above. But this was not done for most of other results except the work in Ref. 5. As was done for Si and Ge (Refs. 11 and 15) the experimental results agree well with the detailed calculations of Debarnardi, Baroni, and Molinari when the instrument function is taken into account. It will be shown below that when the instrument response function is deconvoluted to correct the linewidth of measured Raman

TABLE I. Some experimental and theoretical determination of FWHM of the first-order Raman phonon of diamond at zero temperature.

References	FWHM (cm^{-1})
Krishnan (Ref. 2) (expt., 1946)	2.9
Solin *et al.* (Ref. 3) (expt., 1970)	1.48 ± 0.02
Borer *et al.* (Ref. 5) (expt., 1971)	1.68 ± 0.05
Zouboulis *et al.* (Ref. 7) (expt. fit, 1991)	0.416
Klemens (Ref. 9) (theory, 1966)	0.035
Debernardi *et al.* (Ref. 11) (theory, 1995)	1.01
This work (expt.)	1.103 ± 0.03

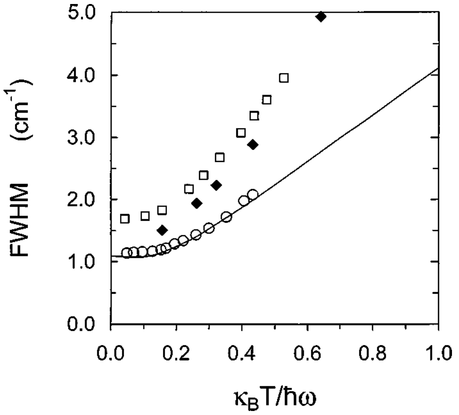

FIG. 2. Linewidth (FWHM) of diamond versus reduced temperature $k_B T/\hbar\omega$ (open circles). The solid line is the theoretical work of Debernardi, Baroni, and Molinari (Ref. 11). For comparison, the solid diamonds and open squares are from Herchen and Cappelli (Ref. 6) and Borer, Mitra, and Namjoshi (Ref. 5).

line, excellent agreement can also be obtained for the case of diamond as compared to the calculations of Debernardi, Baroni, and Molinari.[11]

In Fig. 2, we plot the calculation of Debernardi, Baroni, and Molinari together with our experimental results of the FWHM as a function of reduced temperature. Again for comparison, the solid diamonds and open squares are from Herchen and Cappelli[6] and Borer, Mitra, and Namjoshi,[5] respectively. We see that the agreement of our experiment with the detailed calculation is excellent, the calculated and the experimental linewidth at $T=0$ are 1.01 and 1.1 cm^{-1}, respectively. The present work fills in the gap which previously existed comparing Debarnardi's calculations with the experimental data for diamond, and shows that this theory is applicable to all the the group-IV covalent semiconductors C, Si, and Ge.

B. Temperature dependence of the Raman frequency

The peak position of the first-order Raman mode as a function of temperature is given in Fig. 3 in the temperature range 78–823 K (open circles). Also shown, for comparison, are the experimental results previously reported by Borer, Mitra, and Namjoshi[5] (open squares), Herchen and Cappelli[6] (solid diamonds), Zouboulis and Grimsditch[7] (solid triangles), and Cui *et al.*[8] (solid squares). Our results are in good agreement with those of Ref. 7.

The solid line in Fig. 3 gives the theoretical calculation of the line shift using Eq. (5), which assumes that (i) the Klemens channel model describes well the anharmonic coupling between zone-center phonons and acoustic modes and (ii) the anharmonic coupling excludes the thermal expansion and the quartic terms which are supposed to cancel each other. For the first-order Raman mode of diamond, our fit gives $\omega_0 = 1332.7 \pm 0.03\,\mathrm{cm}^{-1}$ at 0 K. The quoted errors reflect the standard mean squared error between the fit and the data. Taking into account different samples, the error is 0.2 cm^{-1}.

If indeed the anharmonic coupling excludes the thermal-expansion term and the quartic terms (or alternatively these terms cancel each other out), then the real and the imaginary part of the self-energy (which are Kramers-Kronig related)

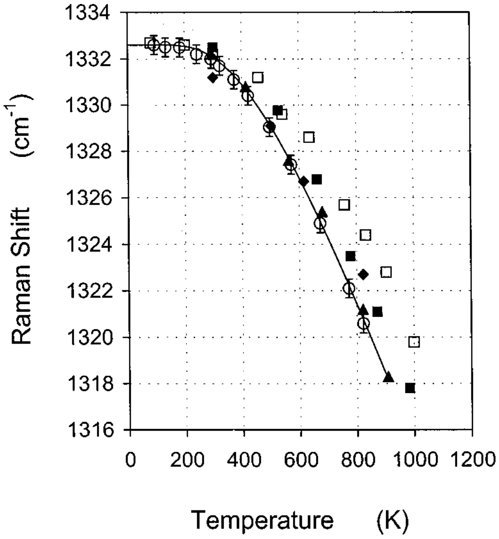

FIG. 3. Temperature dependence of the frequency for the first-order Raman mode in diamond. The solid curve gives the best fit to our experimental results (open circles) using Eq. (5). For comparison, the results from Cui *et al.* (Ref. 8) (solid squares), Zouboulis and Grimsditch (Ref. 7) (solid triangles), Herchen and Cappelli (Ref. 6) (solid diamonds), and Borer, Mitra, and Namjoshi (Ref. 5) (squares) are shown.

should be linearly dependent on each other. As seen in Fig. 4, the linewidth is indeed linearly related to the Raman line shift. This supports the above proposition and implies that the approximation of decay process made here is valid for diamond. Thus two points can be drawn: (i) the cancellation of the thermal expansion by the quadratic anharmonic term is justified. (ii) the linear dependence implies that the Klemens decay channel is the main channel, and there is no need for additional decay channels in our temperature range. It is important to note that we did not observe any shift of the Raman line without a concomitant broadening of the line. Therefore we conclude that for diamond, the dominant origin of the temperature-affected decay of the zone-center phonon is the second-order anharmonic interaction term.

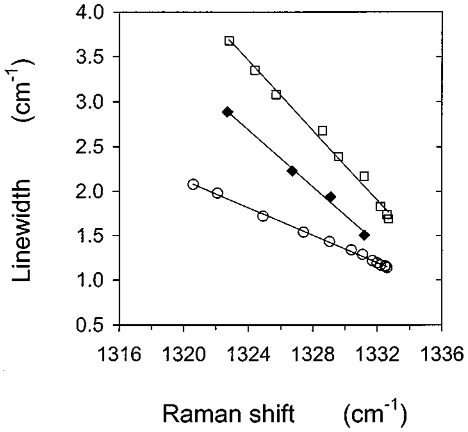

FIG. 4. Linewidth (FWHM) versus Raman frequency in diamond at different temperature. The solid diamonds and open squares are from Herchen and Cappelli (Ref. 6) and Borer, Mitra, and Namjoshi (Ref. 5). The lines are linear least-squares fit to the data.

A calculation of the slope of the line in Fig. 4 would require a complete knowledge of the phonon dispersion curves[19,15] and this is beyond the scope of the present work. However, it should be stressed that a single straight line well describes the linewidth versus peak shift relationship over the entire temperature range examined in this work. This indicates that regardless of the exact functional form of the temperature dependence of linewidth and peak shift, a single decay channel (as described by Klemens) dominates over the whole temperature range. This is in contrast to the results of Balkanski, Wallis, and Haro[14] on the temperature dependence of Raman scattering of Si who had to include the decay of zone-center optical phonons into two and three acoustic phonons to obtain a good agreement between theory and experiment.

V. CONCLUSION

Noncontact temperature measurements using Raman scattering were carefully performed on single-crystal diamond. The extrapolated zero-temperature phonon frequency and lifetime of the first-order Raman mode in diamond are found to be $1332.7 \pm 0.2\,\mathrm{cm}^{-1}$ and $1.103 \pm 0.03\,\mathrm{cm}^{-1}$, respectively. These results are in excellent agreement with *ab initio* calculations made by Debernardi, Baroni, and Molinari.[11] We showed also that the anharmonic effect makes the zone-center Raman phonon of diamond decay into two acoustic modes with opposite momenta belonging to the same branch. This approximation is not valid for other covalent materials such as Si and Ge, where the zone-center phonon decays into acoustic modes from different branches.

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