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Raman scattering in diamond up to 1900 K

E. S. Zouboulis* and M. Grimsditch
Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439

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The temperature dependence of the zone-center optical phonon of diamond has been investigated up to 1900 K using Raman scattering. Our frequencies agree well with the first measurements of the temperature dependence of this mode but are found to fall halfway between those obtained in two later determinations up to 1000 K. Up to ~1000 K, there is a noticeable nonlinearity in the frequency changes; above ~1000 K the frequency change is almost linear with temperature. The measured positions and widths are also compared with theoretical calculations.

INTRODUCTION

Because of potential applications of ceramic materials to situations where they are subjected to high temperatures, there is considerable interest in the properties of materials at high temperatures. Of technological importance are aspects relating to structural stability and mechanical strength. These properties are in turn related to more basic properties such as the normal modes of vibration which provide insight into the microscopic nature of the interatomic forces and, in cases where "soft modes" exist, are directly related to structural phase transitions.

Here we present the results of a Raman-scattering study of the zone-center optical phonon of diamond up to 1900 K. From the basic standpoint diamond is important because it is one of the simplest of all nonmetallic solids and hence provides a good system in which to test theoretical models. Technologically it also has many potential applications that rely on its hardness and stability under extreme conditions of temperature and pressure. Our data on the temperature dependence of the frequency and linewidth of the zone-center optical phonon are compared with previous measurements below 1000 K and also with theoretical calculations.

The temperature dependence of the frequency and linewidth of the zone-center optical phonon of diamond, silicon, and germanium have been calculated by Cowley[1] and Klemens.[2] Cowley used a shell model for his lattice-dynamical calculations: the parameters of the harmonic part of this model were determined from experimental dispersion curves, while the anharmonic part was determined from thermal-expansion data. Within the limits of the shell model Cowley's calculation is complete, in the sense that it considers all possible decay channels for the zone-center optical phonon. Klemens considers only the simplest channel for the decay of the zone-center optical phonon, namely, its splitting into two acoustic phonons of opposite momentum. Using second-order perturbation theory he derives a simple analytic formula for the temperature dependence of the linewidth of the zone-center optical phonon.

Among the materials crystallizing in the diamond structure, Si and Ge have received considerably more attention presumably because of their technological importance. In recent years, however, new fabrication techniques of diamond films which have many potential practical applications have substantially increased the attention being paid to it. Studies of the temperature dependence of the frequency and linewidth of the zone-center optical phonon in Si and Ge have been reported in the literature.[3-5] Hart, Aggarwal, and Lax[3] got good agreement with Cowley's calculation for the frequency shift of the zone-center optical phonon in Si and Ge but not for the linewidth where the calculations gave values higher than the measured values by almost an order of magnitude. To resolve this discrepancy between theory and experiment, a more systematic effort was undertaken for silicon and germanium,[4,5]

Menendez and Cardona[5] infer that the principal decay channel involves the creation of LA-LO phonon pairs, rather than the creation of two LA phonons as postulated by Klemens.[2] Also, in order to explain why Cowley's calculation gives larger linewidths than those obtained experimentally for Si and Ge, they give some qualitative arguments in favor of Weber's adiabatic bond-charge model. They repeated Cowley's lattice-dynamical calculation using Weber's model in the place of the shell model originally used by Cowley. The resulting fit for the temperature dependence of the linewidth agrees reasonably well with their experimental data. Nevertheless, it falls too low by ~20% with respect to the experimental points at the highest temperatures reached in the experiment (900 and 800 K for Si and Ge, respectively).

Balkanski and co-workers[4] included in their lattice-dynamical calculation for Si noncentral interactions and short-range central forces out to fourth neighbors in the harmonic part of the potential energy. For Si they got qualitative agreement for the frequency and linewidth but their measurement of the linewidth at the highest temperature (1300 K) is ~80% larger than the value predicted from their lattice-dynamical model. Their calculation at 1300 K also predicts a frequency shift which is smaller than the measured frequency shift by ~30%. The experimental results for the frequency of the zone-center optical phonon in Si and Ge (Refs. 3–5) essentially agree with each other. For the linewidth, however, there are apparent differences which may be attributed to the different methods used to deconvolute the finite instrumental resolution.

EXPERIMENT AND RESULTS

Our Raman experiments were performed using 4067-Å radiation from a Kr^+ laser and a Spex double monochromator. The furnace, which operates in vacuum or in an inert gas atmosphere, is capable of reaching 2300 K. The temperature was measured with a type-C [W(5 at. % Re)/W/(26 at. % Re)] thermocouple that had been calibrated using the fixed points of melting of a number of metals; we estimate the accuracy of our temperature measurements to be ~10 K.

One of the problems of studying diamond at high temperatures is that it becomes reactive with the refractory metals of the furnace. In a trial run in an argon gas atmosphere our diamond sample almost completely reacted with the tungsten support at a temperature of ~1400 K. Sealing the sample in vacuum in fused silica tubes enabled us to reach 1900 K: at ~1500 K the fused quartz tube collapsed around the sample but did not preclude further measurement. The upper temperature limit was determined by the "blackening" of the silica tube presumably due to condensation of metallic vapors on it. At the highest temperatures reached we did observe some graphitization in the recovered sample, a fact which is not at all surprising in light of the very detailed investigations of this phenomenon reported in the literature.[6]

The problem of blackbody radiation was not as severe as might have been expected; the Raman signal from diamond is sufficiently strong that even at 1900 K it is observable above the thermal background. Figure 1 shows two spectra recorded at room temperature and 1898 K, respectively. It is clear from these spectra that the Raman line has markedly changed in frequency as well as linewidth. (The Raman line positions were always measured relative to a Kr plasma line to avoid any problems of spectrometer tracking.)

Figure 2 shows our measured frequencies (solid circles) as a function of temperature. At room temperature our value agrees well with previous determinations. The figure also contains temperature results previously reported in the literature: Anastassakis, Hwang, and Perry,[7] open circles; Borer, Mitra, and Namjoshi,[8] triangles; Krishnan,[9] crosses; and Solin and Ramdas,[10] plusses. Up to 1000 K our results agree well with those of Krishnan[9] but are in disagreement with the findings of Refs. 7 and 8. The squares in the figure correspond to theoretical calculations by Cowley[1] and will be discussed in the following section. The solid line in the figure is the thermal-expansion contribution to the frequency shift calculated as described below.

Figure 3 shows the linewidth (full width at half maximum) of the Raman line. We have made no attempt to deconvolute the instrumental linewidth (shown by the arrow in the figure) but our results (solid circles) at room temperature are in reasonable agreement with previous

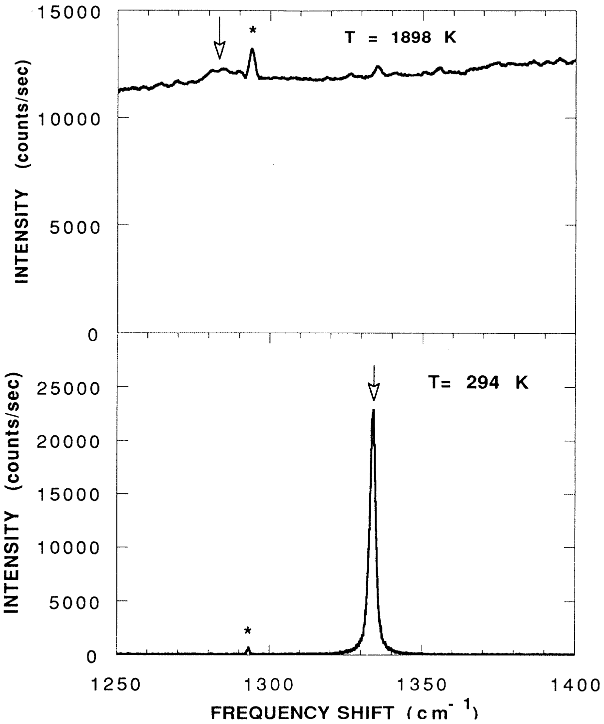

FIG. 1. First-order Raman spectra of diamond obtained in the backscattering geometry at ambient and high temperatures. The arrow indicates the position of the first-order phonon peak, the star indicates the position of a plasma line from the Kr^+ laser. The strong background at high temperatures is due to blackbody radiation from the sample.

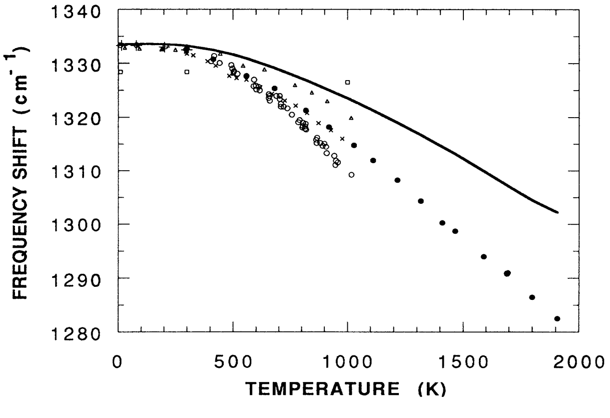

FIG. 2. Temperature dependence of the frequency of the first-order Raman-active mode in diamond. The solid circles are our results, open circles, triangles, crosses, and plusses are experimental results from Refs. 7, 8, 9, and 10, respectively. The squares correspond to the line shift calculations by Cowley (Ref. 1). The solid line represents the thermal-expansion contribution to the phonon frequency calculated as described in the text.

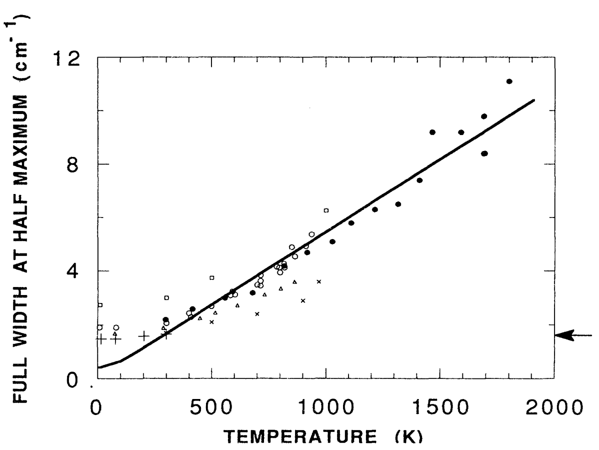

FIG. 3. Temperature dependence of the full width at half maximum for the first-order Raman-active mode in diamond. The solid circles are our results, open circles, triangles, crosses, and plusses are results from Refs. 7, 8, 9, and 10, respectively. The arrow indicates our instrumental resolution: 1.6 cm^{-1}. The instrumental resolutions in Refs. 7, 9, and 10 were 1.0, 1.5, and 0.40 cm^{-1}, respectively. The data from Ref. 8 have been corrected to zero slit width. The squares correspond to the linewidth calculations by Cowley (Ref. 1). The solid line represents the temperature dependence of the linewidth based on a fit using Klemens's model (Ref. 2).

determinations. The open circles, triangles, crosses, and plusses again show the results of Refs. 7–10, respectively. The instrumental resolutions in Refs. 7, 9, and 10 were 1, 1.5, and 0.4 cm^{-1}, respectively. The data from Ref. 8 (triangles) have been corrected to zero slit width. Although the agreement between the different experimental determinations of the linewidths is better than for the frequency of the mode, there are still systematic differences between the various determinations. The squares and the solid line in the figure correspond to theoretical calculations by Cowley[1] and Klemens,[2] respectively, and will be discussed in the following section.

DISCUSSION

The squares in Figs. 2 and 3 correspond to the calculation by Cowley,[1] which predicts a frequency shift for the zone-center optical phonon in Si in good agreement with experiment. In the case of diamond it reproduces the linewidth reasonably well but does not explain the large frequency changes observed on heating. The theories presented in Refs. 4 and 5 qualitatively explained the results on Si, but quantitative agreement was not as good at high temperatures. The solid line in Fig. 3 is based on Klemens's model: it is in good agreement with experiment but it must be pointed out that it does contain one fitting parameter. The model predicts the linewidth (Γ) at a temperature T to be given by

$$\Gamma(T)=\Gamma(0)\{1+2/[\exp(h\omega/2kT)-1]\}\ , \tag{1}$$

where $\omega=1333.5\ \mathrm{cm}^{-1}$(7) is the low-temperature frequency of the zone-center optical phonon of diamond. Fitting this expression to our data leads to $\Gamma(0)=0.416\ \mathrm{cm}^{-1}$. This value is not in good agreement with the value 1.48 cm^{-1} obtained by extrapolation to zero slit width in Ref. 8 (see Fig. 3).

Since existing theories do not satisfactorily explain the temperature behavior of the Raman line of diamond, we attempt below to extract the pure temperature dependence of the frequency (no volume change) from our experimental results. The measured frequency change can be written[11]

$$\Delta\omega=\left[\frac{d\omega}{dT}\right]_V\Delta T+\left[\frac{d\omega}{dV}\right]_T\Delta V\ . \tag{2}$$

The volume dependence of the frequency can be calculated using the mode Grüneisen constant γ which has been measured in a number of investigations: a least-squares fit to all these determinations[12] yields 1.12. The thermal-expansion coefficient $\alpha(T)$ has been measured up to 1700 K;[13] a fit to these results allowed us to extrapolate to 1900 K. With the above assumptions the pure volume dependence of the frequency is given by[8,11]

$$\omega(T)=\omega(0)\exp\left[-3\gamma\int_0^T\alpha(T)dT\right] \tag{3}$$

and is shown by the line in Fig. 2. The difference between our experimental results and this calculation is the pure temperature effect on the frequency and is plotted in Fig. 4. A linear fit through these points yields $(d\omega/dT)_V=(1.21\times10^{-2})\ \mathrm{cm}^{-1}/\mathrm{K}$.

From the results of this investigation we draw the following conclusions.

(a) The line shift of the zone-center optical phonon of diamond up to 1900 K cannot be attributed to thermal-expansion effects only.

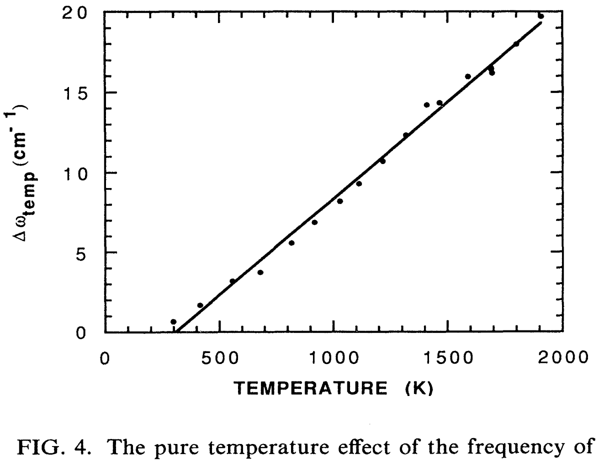

FIG. 4. The pure temperature effect of the frequency of the first-order Raman-active mode in diamond. The solid line is a linear fit through the points.

(b) The pure temperature effect $(d\omega/dT)_V$ is a constant within experimental error in the range 300–1900 K.

(c) Existing lattice-dynamical theories, which have had partial success in describing the high-temperature behavior of the zone-center optical phonon for Si and Ge, do not adequately describe the behavior of diamond. To fully interpret the experimental results it appears that calculations that extend existing models are necessary.

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[*] On leave from the National Technical University of Athens, Greece.

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