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Temperature Dependence of the Long-Wavelength Optical Phonons in Diamond[*]

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We investigate the effects of temperature in the range 10–1000 °K on the frequency and linewidth of the $\vec{q} \simeq 0$ optical phonons in diamond, using Raman-scattering techniques. Comparison is made between the present results and those obtained experimentally and theoretically by other workers. As the temperature increases, the broadening of the line is determined by an increasing number of channels through which the mode decays into pairs of acoustical modes. Beyond 850 °K it is found that the crystal exhibits higher-order anharmonicity. It is also established that the frequency shift is largely due to thermal expansion, and that the scattering occurs under conditions of phonon-population equilibrium.

I. INTRODUCTION

Diamond exhibits one triply degenerate long-wavelength optical mode (referred to as "mode" from now on) which is Raman active and normally infrared (ir) inactive. The mode is a strong scatterer and its frequency has been well established through Raman-scattering techniques for a long time.[1] The frequency has also been confirmed by neutron[2] and ir experiments.[3] The study of the temperature dependence of Raman-scattering spectra of silicon[4] and germanium,[5] the other two common diamond-type crystals, has led to interesting conclusions regarding the anharmonicity of these crystals, and the validity of the existing lattice-dynamical theoretical models.[6,7] A similar study of the temperature dependence of the Raman spectrum of diamond, mainly in first order, was made by Krishnan[1] long before any theoretical work had been attempted. A complete account of the temperature dependence of diamond's second-order Raman spectra below 300 °K was recently reported by Solin and Ramdas.[8]

We report in this paper our most recent results of the investigation of the temperature dependence of diamond's first-order Raman scattering, in the range 10–1000 °K. The differences between the present results and those obtained by Krishnan appear to be relatively small. However, the improved Raman experimental data indicate that the applicability of the existing theoretical models needs to be reexamined as the agreement between theory and experiment can be considered only as partially satisfactory.

II. EXPERIMENTAL

The measurements were taken using a Spex-1401 double-grating spectrometer and photocounting techniques. The type-IIa diamond sample was kindly supplied by the S. Africa Diamond Research

Center. Its dimensions were 9.6×2.3×1 mm^3 and its orientation was along the [$\bar{1}$10], [11$\bar{2}$], and [111] axes, respectively. For the low-temperature measurements the sample was attached to the copper cold-finger of a standard metal Dewar. For the high-temperature measurements an evacuated cell was used. The sample was wrapped with a piece of metal foil leaving a small window for the beams. The temperature was varied between 300 and 1000 °K by adjusting a current through the foil. An iron-constantan thermocouple in contact with the sample at the foil window was used to measure the temperature (within at most ±10 °K at the highest-temperature range).

To simulate the orientation conditions of the work in Si[4] and Ge,[5] we performed the scattering measurements in a backward configuration along the [111] axis. Incident and scattered radiation were polarized along the [11$\bar{2}$] axes. A Spectra-Physics model-125 He-Ne laser was used in these experiments. The power level was kept down to 25 mW at the sample and local heating of the sample was found to be negligible because of the transparency of diamond at 6328 Å. Several measurements were taken for each temperature at different times. Throughout the whole experiment the entrance and exit slit widths were fixed at 38 μ with the intermediate slit at 100 μ. An instrumental resolving power of 1 cm^{-1} is estimated for the present frequencies.

III. RESULTS ON THE LINEWIDTH

Figure 1 shows a summary of the present results on the *observed* (uncorrected) full width at half-intensity, for the Raman-active mode in diamond. The results of other workers are also included for comparison. Krishnan's "width vs *T*" curve is shifted upwards by 1.0–1.6 cm^{-1} and its slope above 300 °K is smaller in general. It is very likely that the above consistent differences in the width are due to the different experimental conditions involved, that is, instrumental resolving power, etc. The point *S* at 300 °K indicates the value obtained by Stenman under conditions nearly identical to the present ones.[9] Solin's data below 300 °K are also shown in Fig. 1, taken under conditions of high resolution.[8] The slope of his curve agrees with the present results. The slope on the other hand inferred from Krishnan's points by extrapolation below 300 °K appears to be steeper.

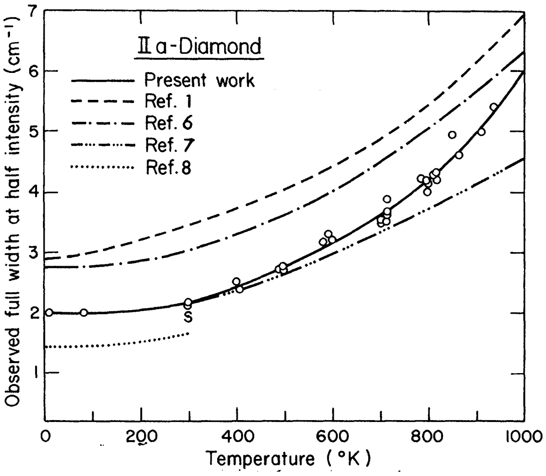

FIG. 1. Temperature dependence of the observed (uncorrected) linewidth of diamond. Theoretical and experimental results of other workers are included. The point designated by "S" at 300 °K indicates the value reported by Stenman (Ref. 9). Instrumental slit width, ~1 cm^{-1}.

In Ref. 3 the width of the line was obtained through electric-field-induced ir absorption measurements at 300 and 77 °K. The symmetry of this effect is identical to that of the intrinsic first-order Raman scattering, inasmuch as one can look upon the former effect as a Raman-scattering effect with the electric field of the scattered radiation replaced by an externally applied static electric field with the same polarization. The values of 1.75 and 1.50 cm^{-1} were obtained in Ref. 3 for the linewidth at 300 and 77 °K, respectively, using the very same diamond sample presently used. The incident and applied fields were polarized parallel to each other, as in the present case, and the instrumental slit width was 0.5 cm^{-1}. Considering the difference in the instrumental slit width in the two experiments (Ref. 3 and present experiment), i.e., ~0.5 cm^{-1}, the agreement between the above values and those from Fig. 1 (2.20 and 2.00 cm^{-1}) must be considered as excellent. It is emphasized that, although the physical and symmetry aspects underlying the two experiments (the field-induced ir absorption and the intrinsic first-order Raman scattering) are identical, the experimentation involved is entirely different (the former was a transmission experiment performed in the ir, the latter was a scattering experiment performed in the visible).

Two independent theoretical curves are shown in Fig. 1. The one by Cowley[6] is based on the assumption that the linewidth of the mode is determined from its coupling through anharmonicity to all possible pairs of acoustical phonons throughout the whole Brillouin zone. Klemens instead considers only one channel of decay of the mode into two acoustical phonons, through a process satisfying energy and momentum conservation.[7] It can then be shown that the width of the mode at temperature *T* is given by[7]

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

where $\Gamma(0)$ is the width at 0 °K, and $x=\hbar\omega_0/2kT$ with ω_0 designating the mode frequency.

In Si, Cowley's points did not fit the data, even after normalization at low temperatures. On the other hand, Klemens's model, i.e., Eq. (1), gave very good agreement with the data.[4] On this basis, it was reasonably concluded that the mode decayed exclusively to two longitudinal acoustic (LA) phonons, each of frequency $\omega_0/2$ and with equal and opposite momentum.

In Ge, with the normalization to the experimental points made at 300 °K rather than 0 °K, Cowley's and Klemens's results agree with each other but deviate from the experimental data.[5] It was then suggested that "intrinsic softening" of the covalent bonds might be the reason for the over-all discrepancy in Ge.[5,10] More recent measurements on the linewidth of Ge give better agreement between theory and experiment.[11]

In the present case of diamond, we plotted the theoretical curves without any normalization, except that of $\Gamma(0)$, as required by Eq. (1). The behavior of the linewidth in different regions of temperature (Fig. 1) is as follows: (i) 0–500 °K; here the two theoretical models are in agreement with the present data, apart from a consistent upward shift (~ 0.8 cm^{-1}) exhibited by Cowley's curve. The latter is very likely due to overestimation of the three-phonon coupling constant involved in this particular model. It is therefore reasonable to conclude that the decay process primarily involves one pair of LA phonons,[2] as required by Klemens's model. The contribution from decay into pairs of acoustical phonons from throughout the Brillouin zone is accordingly negligible, in the region 0–500 °K. (ii) 500–850 °K; in this region the experimental data and Cowley's results continue to agree while Klemens's curve remains consistently lower. The obvious explanation for this is that as T increases more channels of decay are involved in the process, thus making Cowley's model more realistic than Klemens's. (iii) $T > 850$ °K; the observed width increases faster than as required by Cowley's model. It appears that the limit has been reached where the anharmonic approximations involved in Cowley's calculations are no longer sufficient. Higher-order anharmonicity should be taken into consideration.

IV. RESULTS ON MODE FREQUENCY

The temperature dependence of the frequency of the mode is shown in Fig. 2. The frequency measurements were based on the frequency of the excitation line and, alternatively, on the observed absolute frequencies of the Stokes and anti-Stokes components. For moderate temperatures (450–750 °K) the agreement with Krishnan's data is good. Below and above this region however, there are noticeable differences, particularly in the high-temperature region. The flattening of the curve towards 0 °K is broader than that observed in Si[4] and Ge.[5] This seems to be related to the fact that the Debye temperature for diamond ($T_D \geq 1800$ °K) is far higher than that of Si and Ge (~ 680 and 370 °K, respectively[12]).

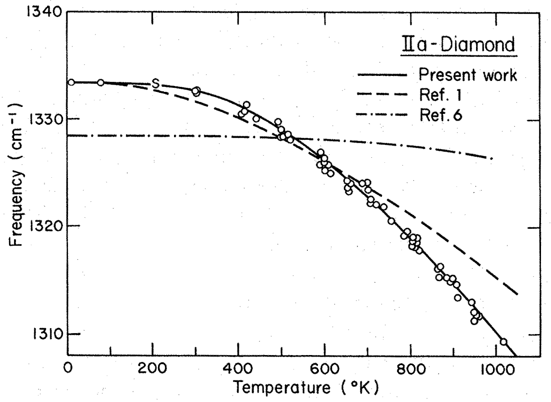

FIG. 2. Temperature dependence of the mode frequency (here measured in wave-number units cm^{-1}) in diamond. The value at 200 °K (designated by "S") was taken from Ref. 8.

Cowley's theoretical model considers three possible anharmonic contributions to the frequency shift: (i) a term due to thermal expansion; (ii) a cubic anharmonic term taken in second order in the expansion of the crystal Hamiltonian; and (iii) a quartic anharmonic term, in first order. Only the second term is supposed to contribute to the width of the mode, whereas all three terms contribute to the frequency shift. Actually, the first and third terms simply give rise to a constant frequency shift. The contributions to the shift arising from these two terms are not considered in Cowley's calculations as being nearly equal and opposite.[12,13] The resulting temperature dependence of the frequency is in very good agreement with the experimental data in the case of Si,[4] apart from an over-all downward parallel shift of the whole curve by ~ 11 cm^{-1} (not indicated in Fig. 2 of Ref. 4). In Ge,[5] the agreement is satisfactory only in the range of $T \geq 300$ °K, when Cowley's results are normalized at 300 °K.

In the case of diamond, the theoretical results shown in Fig. 2 are far different from the present data. The good agreement obtained for Si and Ge, and the fact that the same model gave consistent results for the linewidth of diamond, indicate that the approximations within the model rather than the model itself should be held responsible for the large differences of Fig. 2. We attempted to calculate the effect of the thermal expansion alone, based on a related discussion in Krishnan's work.[1] We used the well-known expression

$$\gamma_{1332} = \frac{d\,(\log\omega)}{d\,(\log V)} = \frac{\omega_2 - \omega_1}{3\alpha\omega_2\,(T_2 - T_1)} \quad , \tag{2}$$

where γ_{1332} is the mode Grüneisen parameter, V is the volume of the crystal, and α is the linear coefficient of thermal expansion. $\omega_2 - \omega_1$ indicates the frequency shift due to thermal expansion alone.

Krishnan's attempt to attribute the entire observed shift of his measurements to thermal expansion effects led to a temperature-dependent value for γ_{1332}, i.e., 6.4–1.7 for $T = 100$–800 °K.[1] However, according to Mitra *et al.*[14] the value of γ_{1332} is 0.94 and within the quasiharmonic approximation is expected to be independent of temperature. We applied Eq. (2) using $T_2 = 0$, $\omega_2 = 1333.5$ cm^{-1}, and the values of $\omega_1(T_1)$ from Fig. 2. For 3α, we used the same set of values used by Krishnan for $T \geq 300$ °K,[1] and, independently, the values reported by Novikova.[15] In the range 300–800 °K, we obtained the nearly constant values of 0.95 and 1.10, respectively, for γ_{1332}, within $\leq 15\%$. We did not extend the calculation below 300 °K because the shifts in this region are of the same order as the experimental error. In view of the results of Ref. 14, we conclude the following: (i) Nearly the entire observed shift is due to the thermal expansion of the crystal; (ii) due to the importance of the thermal-expansion mechanism, Cowley's calculations cannot agree with the experimental results; according to Dolling and Cowley the thermal-expansion contributions are cancelled by an equal and opposite contribution due to the quartic term.[6,12]

V. STOKES TO ANTI-STOKES RATIO

The ratio of intensities of the Stokes and anti-Stokes components is expected to depend on T as described by Bose-Einstein statistical considerations, under phonon-population equilibrium. The ratio is given by

$$I_S/I_A = e^{\hbar\omega_0/kT} \tag{3}$$

and is plotted in Fig. 3 (solid line). We measured this ratio as a function of temperature. Because of the large value of ω_0, it was not possible to obtain values for $T < 300$ °K. Since the difference in the absolute frequencies of the Stokes and anti-Stokes lines is large (~0.33 eV) we made sure that the observed ratios were normalized to identical instrumental response. Furthermore, the ω^4 normalization introduces another fundamental correction[16] (in this case of the order of 2). The experimental points of Fig. 3 have been corrected for all the above factors. The over-all agreement is very good, indicating that the scattering occurs under conditions of equilibrium of the phonon population.

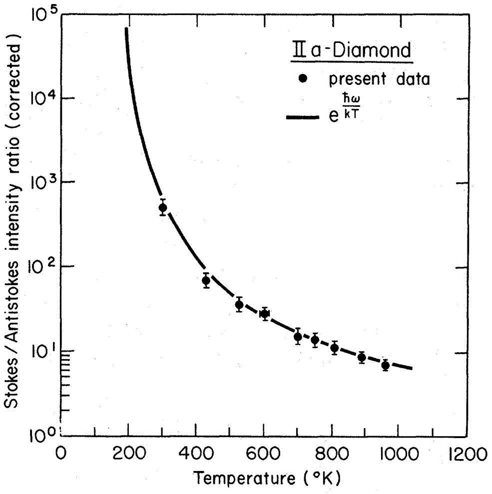

FIG. 3. Corrected observed ratios of the Stokes and anti-Stokes intensities as a function of temperature, and comparison with the theoretical curve based on the assumption of thermal equilibrium.

VI. CONCLUDING REMARKS

The frequency, linewidth, and Stokes to anti-Stokes ratio have been measured as a function of temperature in the range 10–1000 °K, for IIa-type natural diamond. The present results are in partial agreement with those available in the literature. Comparison of the present results on the linewidth, to those obtained through theoretical models based on anharmonicity, allowed us to determine which patterns of the mode decay occur in the different temperature regions. The observed shifts of the mode frequency are found to be essentially determined by the thermal-expansion contributions, in disagreement with theory. This fact emphasizes the basic differences in the anharmonic behavior between diamond and Si and Ge, as previously noted.[17,18] The Raman scattering occurs under phonon-population equilibrium conditions, as indicated by the observed Stokes to anti-Stokes intensity ratios. With the Debye temperature of diamond being far above the temperature range of the present measurements, we did not consider worthwhile fitting the present data to a classical oscillator model. Two more aspects which we think ought to be investigated with variable temperature are the second-order spectra, and the asymmetric shape of the first-order Raman band. Information obtained through either of these experiments may be particularly useful to theorists for establishing final views on the lattice-dynamical properties of these materials.

Note added in proof. Parallel to the present work, an independent group of workers has recently reported results of a similar investigation.[19] Although there are some differences in the experimental data, the over-all qualitative conclusions are in agreement with the present ones. Some results of earlier measurements also appear in Ref.

20.

Finally we would like to comment on the interpretation of Cowley's values on the linewidth. We presently treat these values[6] as *half-width at half-intensity*, based on Table 7 of Ref. 12. Other workers have taken these values as *full width at half-intensity*. It is essential to use the correct interpretation of these values, inasmuch as a factor of 2 affects the conclusions derived from the comparison of theory and experiment, as per Fig. 1.

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Isolated Interstitials in Silicon[†]

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An isolated interstitial in silicon at the nominal site is investigated using a procedure based on the expansion of the wave function in terms of the Wannier functions of the perfect crystal and using a pseudopotential for the defect potential. Scattering phase shifts are calculated for states within the valence band and a search is made for bound states within the band gap. We discover that there is no bound state in the band gap associated with this defect. The change in the one-electron energy arising from the interstitial is calculated and combined with the corresponding quantity for a single vacancy. We find this major contribution to the formation energy of the vacancy interstitial pair to be 13.6 eV.

I. INTRODUCTION

An imperfection or an impurity in a semiconductor may produce a state with an energy within the band gap of the crystal. A general method of study of these defect states and of the change in the density of states was given by Callaway.[1,2] In this approach, the wave function of the defect state is expanded in terms of the Wannier functions for the perfect crystal. Matrix elements on the Wannier-function basis are formed both for the defect potential and the Green's function. Solutions of a determinantal equation yield the bound state. The scattering phase shifts defined in terms of real