PHYSICAL REVIEW B VOLUME 15, NUMBER 12 15 JUNE 1977

Linewidth of the sharp two-phonon Raman peak in diamond*

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(Received 28 June 1976)

The sharp peak in the second-order Raman spectrum of diamond has been studied at temperatures between 4 and 300°K. We find its width to be 4.2 ± 1 cm^{-1} and its peak intensity, relative to the second-order feature at 2450 cm^{-1} to be 0.37 ± 0.01, both being temperature independent. These results are in good agreement with recent predictions of Tubino and Birman deduced from the bond polarizability model without anharmonicity.

In 1970, Solin and Ramdas reported a detailed Raman-scattering study of diamond.[1] They found that at 300 °K, the sharp peak near the high-frequency cutoff of the second-order Raman spectrum, whose existence has first been noted by Krishnan in 1946,[2] occurs at 2667 cm^{-1}, approximately 2 cm^{-1} higher than twice the frequency of the first-order Raman line at 1332 cm^{-1}. They found that the sharp peak is strongly polarized with symmetry Γ_1^+, depends linearly on the scattering volume, and is qualitatively independent of temperature between 20 and 300 °K. (Solin also found that the sharp peak still appears at 1200 °K.)[3]

Cohen and Ruvalds interpreted the sharp peak as a two-phonon bound state, split off the top of the two-phonon continuum by repulsive anharmonic phonon-phonon interactions.[4] This interpretation was further discussed by Ruvalds and Zawadowsky.[5] Recently, however, the two-phonon bound-state interpretation has been questioned, and the possibility has been raised that the sharp peak may be an ordinary two-phonon overtone, reflecting the detailed structure of the two-phonon density of states.[6]

Bond-polarizability calculations by Go, Bilz, and Cardona[7] and by Tubino and Piseri[8] predicted a sharp peak at the cutoff of the two-phonon spectrum without inclusion of anharmonicity. Go, Bilz, and Cardona asserted that "our calculation represents well the frequency of the experimental peak (slightly above $2\omega_{\text{Raman}}$) as well as its shape," although from their histogram, the grid of the calculation appears to have been too coarse to justify this assertion. Tubino and Birman[9,10] subsequently computed the dispersion curves predicted by the bond-polarizability model, and found that, although the phonon energy rises by about 2 cm^{-1} at $q/\sigma_{\max} \sim 0.3$ in the [100] direction, the predicted sharp peak is produced by a fluted F_2 critical point at the Γ point, and therefore corresponds to a pair of zone-center Γ_{25}^+ phonons. In this harmonic calculation, the position of the predicted sharp peak was exactly twice the one-phonon frequency, leaving the source of the 2-cm^{-1} shift unresolved, but presumably due to anharmonicity.[9]

Tubino and Birman have refined their calculation, and computed the second-order Raman spectrum with a resolution of 0.67 cm^{-1}, indicating a width for the sharp peak of ~5 cm^{-1} and a peak intensity relative to the two-phonon feature at 2450 cm^{-1} of about $\frac{1}{3}$.[9,11]

Since the temperature dependence of the sharp peak should be an important experimental parameter against which to test the competing theories, and no quantitative linewidth measurements have been reported in the literature, we have measured the linewidth and intensity of the sharp peak at several temperatures between 4 and 300 °K. Our experiments were performed on a $2 \times 2 \times 5$ mm South African type-I natural diamond cut along principal axes. The sample was mounted on the cold finger of an Air Products "cryo-tip" Dewar. Raman spectra were taken in a right-angle scattering geometry, using 150 mW of 4880-Å laser excitation propagating parallel to the 5-mm axis. The Raman scattered light was analyzed using a Spex 1401 double-grating spectrometer and photon counting electronics, and recorded on a strip-chart recorder. The frequency shift and shape of the first-order Raman line and the sharp peak in the second-order spectrum were measured at room, liquid nitrogen, and liquid helium temperatures. A resolution of 0.5 cm^{-1} was used to measure the first-order line, and a resolution of 1.8 cm^{-1} was used for the sharp peak.

TABLE I. Temperature dependence of the half width and position of the first-order Raman line of diamond.

Temperature	Line position (cm^{-1})	Uncorrected width	Corrected width [a]
Room	1333.0 ± 0.5	1.7 ± 0.1	1.2 ± 0.2
Liquid nitrogen	1333.5 ± 0.5	1.7 ± 0.1	1.2 ± 0.2
Liquid helium	1333.5 ± 0.5	1.7 ± 0.1	1.2 ± 0.2

[a] Corrected by simple subtraction of instrumental width

TABLE II. Temperature dependence of the half width and position of the second-order Raman line of diamond.

Temperature	Line position (cm^{-1})	Uncorrected width	Corrected width
Room	2669 ± 1	6.0 ± 1	4.2 ± 1
Liquid nitrogen	2770 ± 1	6.0 ± 1	4.2 ± 1
Liquid helium	2770 ± 1	6.0 ± 1	4.2 ± 1

The results of our measurements are shown in Tables I and II, and Figs. 1 and 2. A frequency of 1333.0 ± 0.5 cm^{-1} and a full width at half-maximum of 1.7 ± 0.1 cm^{-1} was measured for the first-order line at room temperature. These results are in good agreement with the values 1332.5 ± 0.5 cm^{-1} and 1.65 ± 0.02 cm^{-1} obtained by Solin and Ramdas[1] at room temperature, using a resolution of 0.4 cm^{-1}.

In Fig. 2, three spectra of the sharp peak are shown, indicating a width at half-maximum of approximately 6 cm^{-1} and a center frequency of 2269 ± 1 cm^{-1} at 300 °K, which is 3 cm^{-1} higher than twice the measured frequency of the first-order line. Within our experimental accuracy, very little change in the shape, frequency, or relative inten-

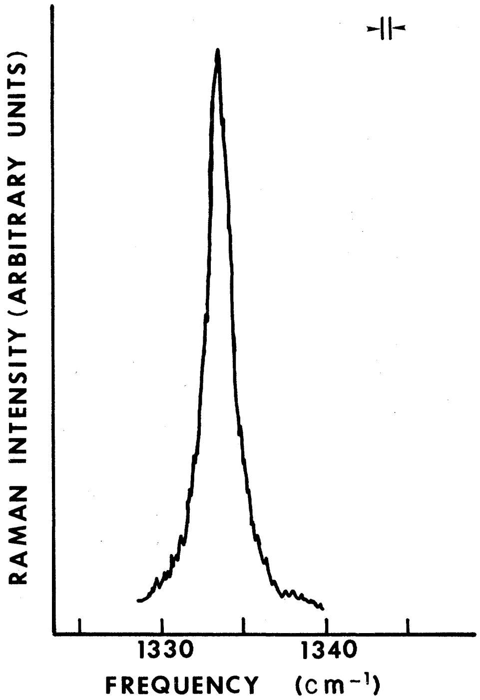

FIG. 1. Raman spectrum of the first-order line in diamond, taken with an instrumental resolution of 0.5 cm^{-1} at room temperature, showing a line positon of 1333 cm^{-1} and an uncorrected width of 1.7 cm^{-1}.

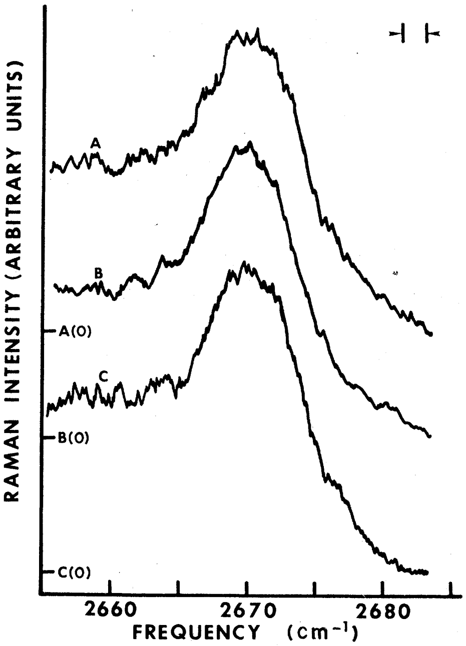

FIG. 2. Three Raman spectra of the sharp peak in the second-order spectrum of diamond taken with an instrumental resolution of 1.8 cm^{-1}, approximately at: (a) room temperature, (b) liquid-nitrogen temperature, and (c) liquid-helium temperature. The spectra are displaced vertically with respect to each other for clarity. $A(0)$, $B(0)$, and $C(0)$ indicate the zero-point reference.

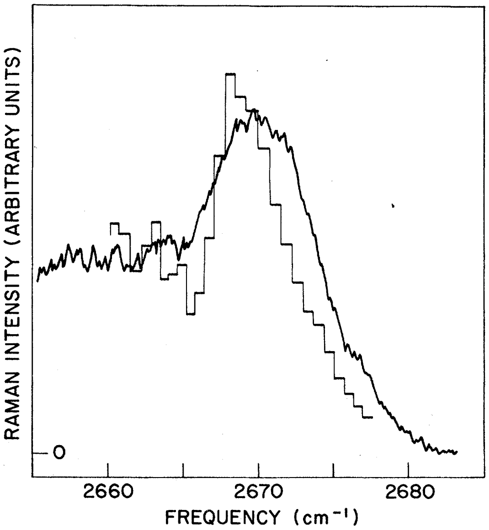

FIG. 3. Experimental Raman spectrum of diamond at 4.2 °K in the cutoff region compared with theoretical histogram of Tubino and Birman (Ref. 11). Experimental resolution: 1.8 cm^{-1}. Theoretical resolution: 0.67 cm^{-1}.

sity with respect to other second-order Raman features was observed as a function of temperature. The intensity of the sharp peak relative to the second-order feature at 2450 cm^{-1} was remarkably constant at 0.37 ± 0.1 between 4.2 and 300 °K. In Fig. 3, we compare the 4.2 °K spectrum in the region of the high-frequency cutoff with the theoretical prediction of Tubino and Birman.[11] The agreement, although not perfect, is quite good.

In conclusion, we have found that the linewidth and intensity of the sharp peak in the second-order Raman spectrum of diamond are effectively temperature independent between 4 and 300 °K, a result which appears difficult to reconcile with the bound two-phonon picture which includes a binding energy of only 2.5 °K.[12] On the other hand, although our results are in good agreement with many of the predictions of the bond-polarizability calculation, it remains to be seen whether these calculations can be refined sufficiently to explain the 3-cm^{-1} shift between the sharp peak and twice the first order Raman frequency.

ACKNOWLEDGMENTS

We are grateful to J. L. Birman for suggesting this problem to us and for numerous helpful discussions, to R. R. Alfano for generously lending us the diamond used in this experiment, which was on loan from Dr. P. Caveney of De Beers Diamond Research Laboratory of South Africa, and to R. Tubino for Fig. 3.

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*Work supported by the NSF.

†Supported in part by the National Fellowship Fund.

‡Supported in part by the Alfred P. Sloan Research Foundation.

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[11] R. Tubino and J. L. Birman, following paper, Phys. Rev. B 15, 5843 (1977).

[12] However, the width of the first-order Raman line is also essentially temperature independent in this range [cf. E. Anastassakis, H. C. Hwang, and C. H. Perry, Phys. Rev. B 4, 2493 (1971)].